Supporting Information

"Click-Switch" – One-step conversion of organic azides into photochromic diarylethenes for the generation of light-controlled systems

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Content

1. Supplementary Figures, Schemes and Tables

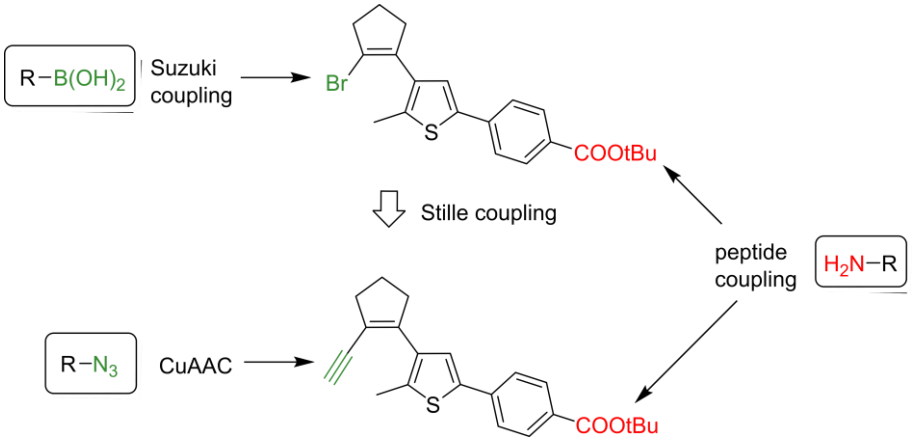


Fig. S1 Schematic illustration of the potential modular assembly options of the designed precursor molecules. In addition to the introduction of the second aryl ring by cross-coupling or CuAAc, the system could be modified by amide coupling with various functionalities like fluorophores, water-soluble groups or further linkers.

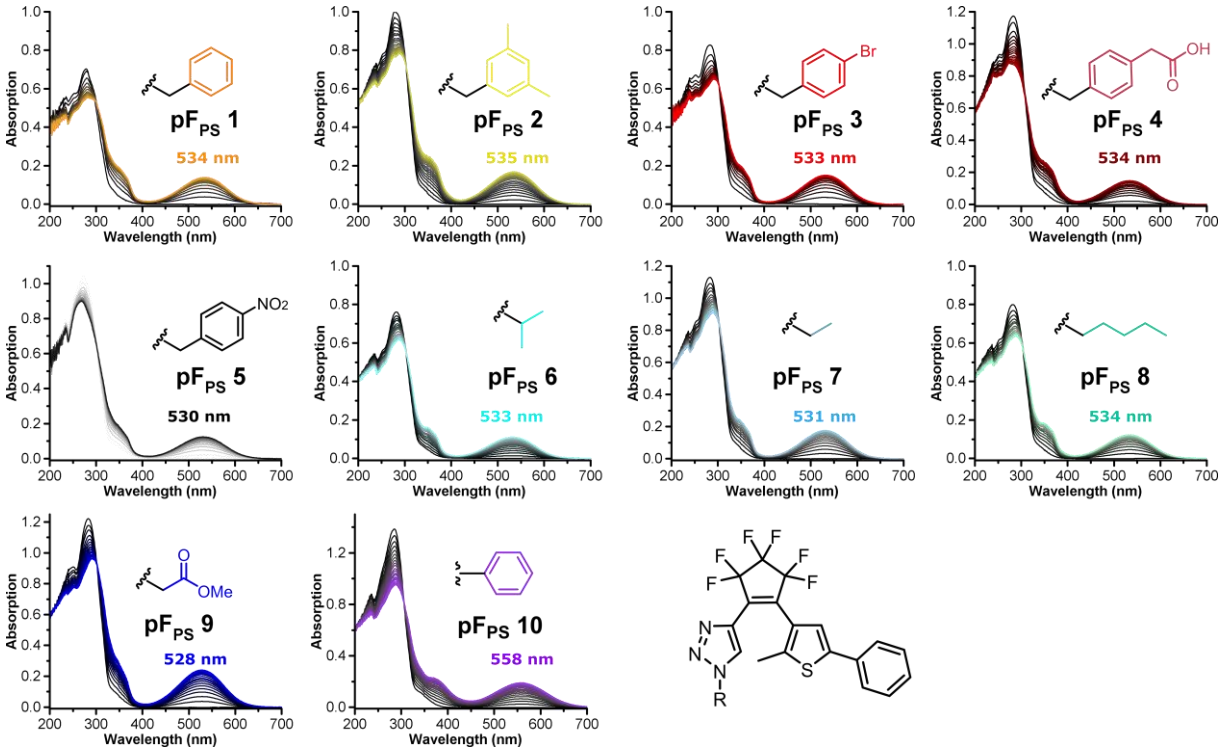


Fig. S2 Time-dependent changes in the absorption spectra of chloroformic solutions of the photoswitches shown in Fig. 4 (60 µM) during UV light irradiation (310 nm, LED).

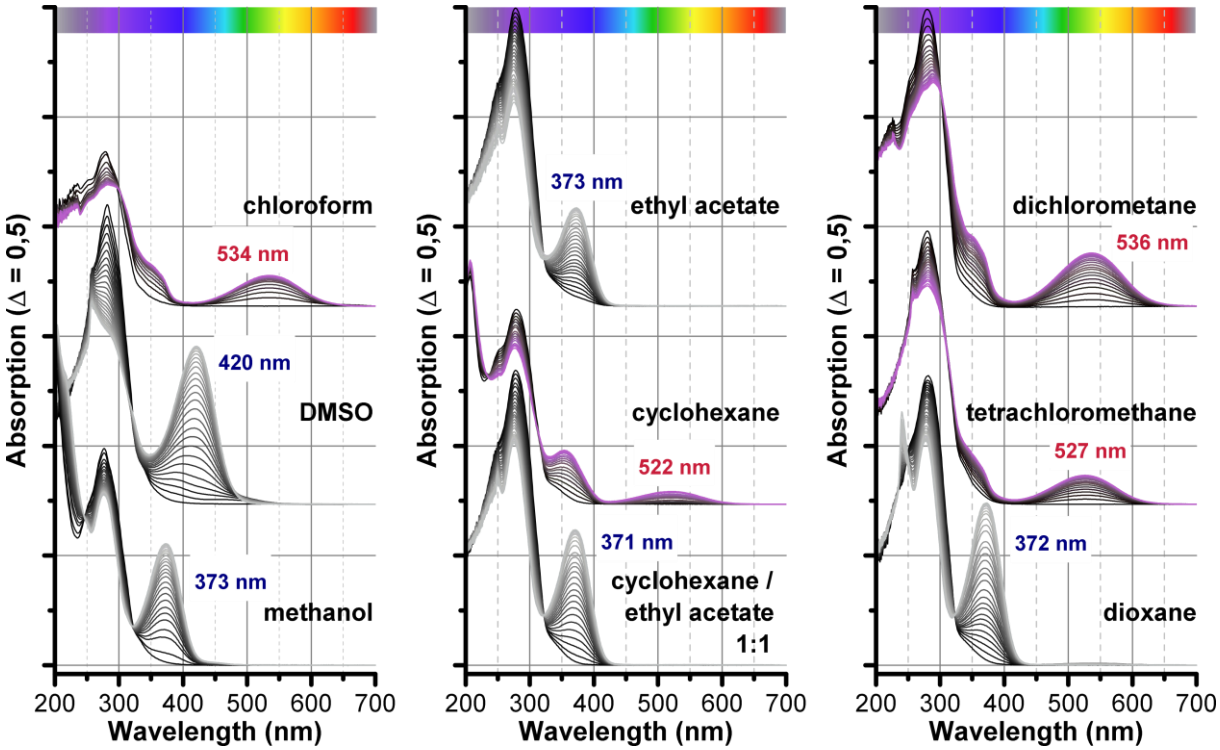


Fig. S3 Time-dependent changes in the absorption spectra of **pF$_{PS}$ 1** (60 µM) in different solvents during UV light irradiation (310 nm, LED). Magenta: reversible photochromic reaction and formation of the visible absorption band of the closed-form isomer, grey: irreversible reaction and formation of a new specific UV band.

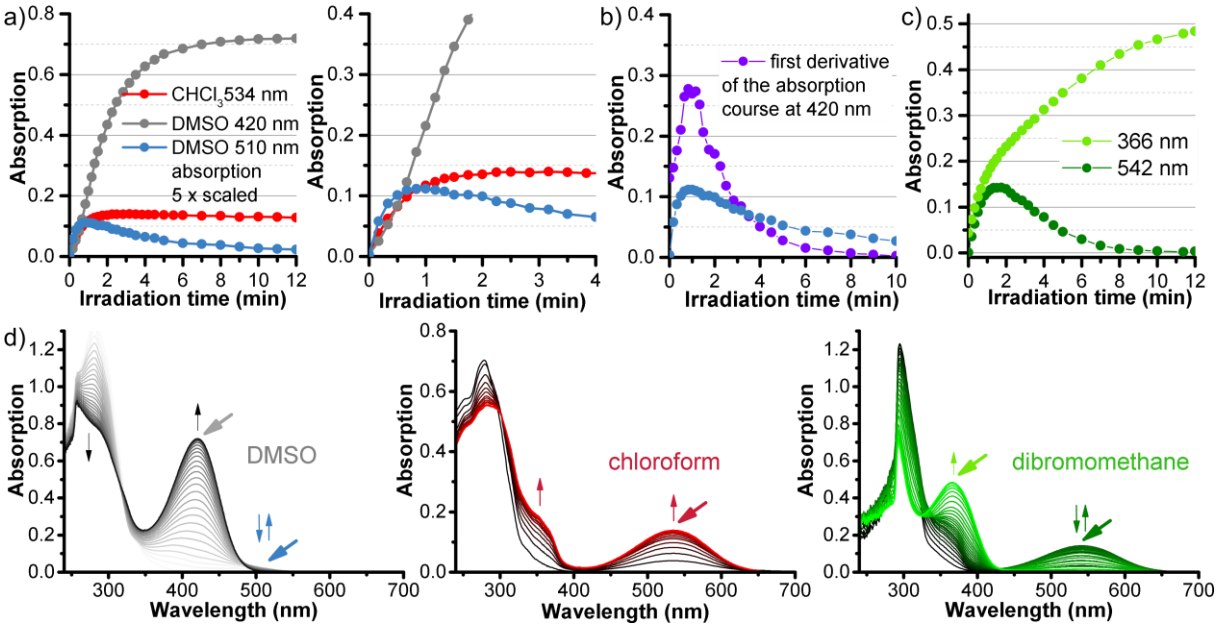


Fig. S4 Kinetics of the UV light-induced reaction (310 nm, LED) of **pF$_{PS}$ 1** in different solvents (60 µM): a) Kinetic trace of the absorption (wavelengths specified in the picture) during irradiation in DMSO, right panel: magnification) b) Comparison of the kinetic trace of the visible absorption in DMSO (510 nm, blue curve) and the first derivative of the absorption at 420 nm, c) kinetic traces of the VIS absorption (366 and 542 nm) in a dibromomethane solution, d) Time-dependent changes in the absorption spectra in different solvents, the wavelengths of the absorption curves shown in a, b and c are marked with slanted arrows.

The kinetics in DMSO shows the formation and decay of a faint band at 510 nm (**Fig. S4, a** and **b**, upscaled by factor 5), which is well correlated to an initially hampered rate of formation of the 420 nm band. In dibromomethane (**Fig. S4**, **c**) the reaction rates for the formation of the UV band and the vis band are correlated. This supports the assumption that in DMSO and dibromomethane a specific side reaction from the initially formed closed isomer takes place.

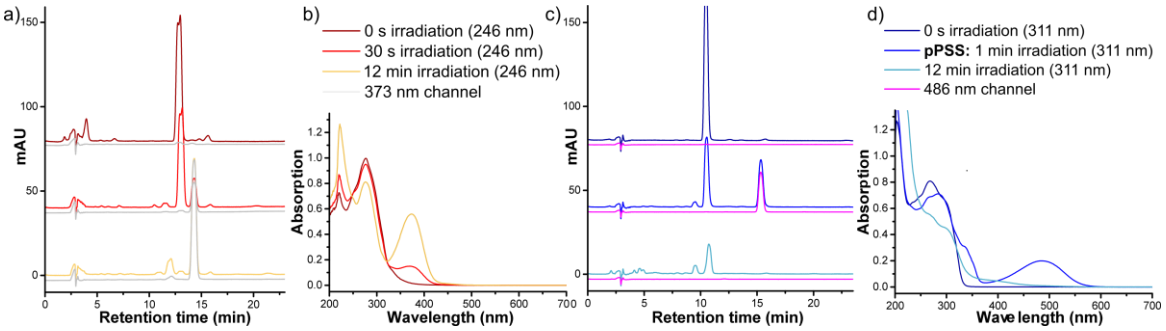


Fig. S5 Comparison of the reaction progress of **pF$_{PS}$ 1** (red, panel a,b) and **pH$_{PS}$ 1** (blue, panel c,d) in methanolic solutions (60 µL).

a and c: HPLC analysis of the reaction mixtures measured at selected time points (see color code) during the UV light irradiation:

1. no irradiation (original solutions),
2. significant conversion,
3. 12 minutes to enforce bleaching (**pH$_{PS}$ 1**), complete conversion (**pF$_{PS}$ 1**),

b and d: absorption spectra of the reaction mixtures measured correlatively to the HPLC injections. For experimental details see SI chapter 2.1. – 2.4.

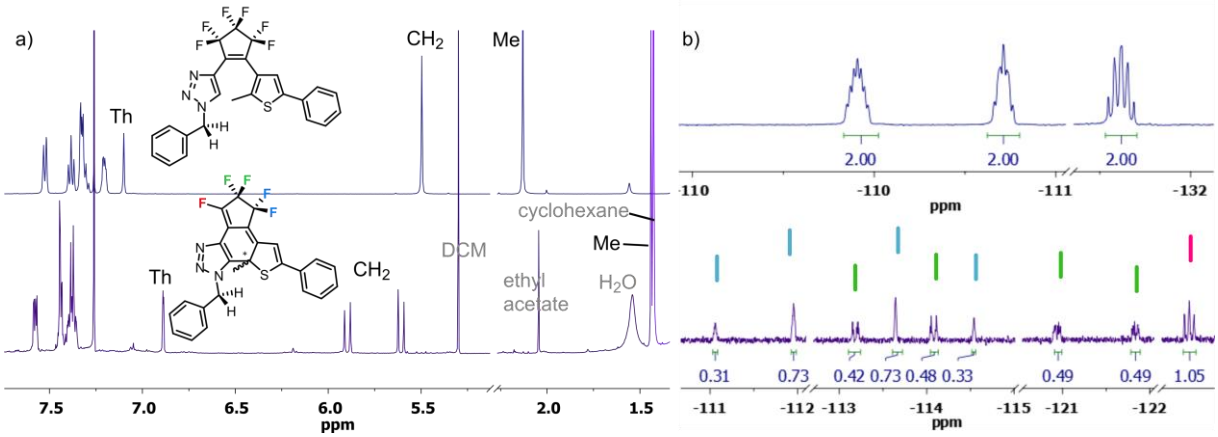


Fig. S6 a) ^{1}H- (500 MHz) and b) ^{19}F-NMR-spectra (282 MHz) of the isolated side product that is formed during the irradiation of **pF$_{PS}$ 1** in methanol (see SI chapter 2.5.5.).
The ^{1}H-NMR spectrum of the isolated side product (bottom) shows diasterotopic signals of the benzylic CH_2-group which shows a homotopic singlet signal in the open-ring isomer (top). This indicates a structure of the side product in which the (former) aryl groups are connected in a rather rigid manner. The similarity of the chemical shift of the diastereotopic signal to that of the homotopic signal may indicate the restoration of the aromatic triazole through the HF-elimination, and this consideration would confirm the structure **pF-BP**. The ^{19}F-NMR spectrum shows one triplett signal and two pairs of diasterotopic signals. This pattern can be related to an F-eliminated hexafluorocyclopentene.
Th: thiophene protons, CH_2: methylene group, Me: methyl group.

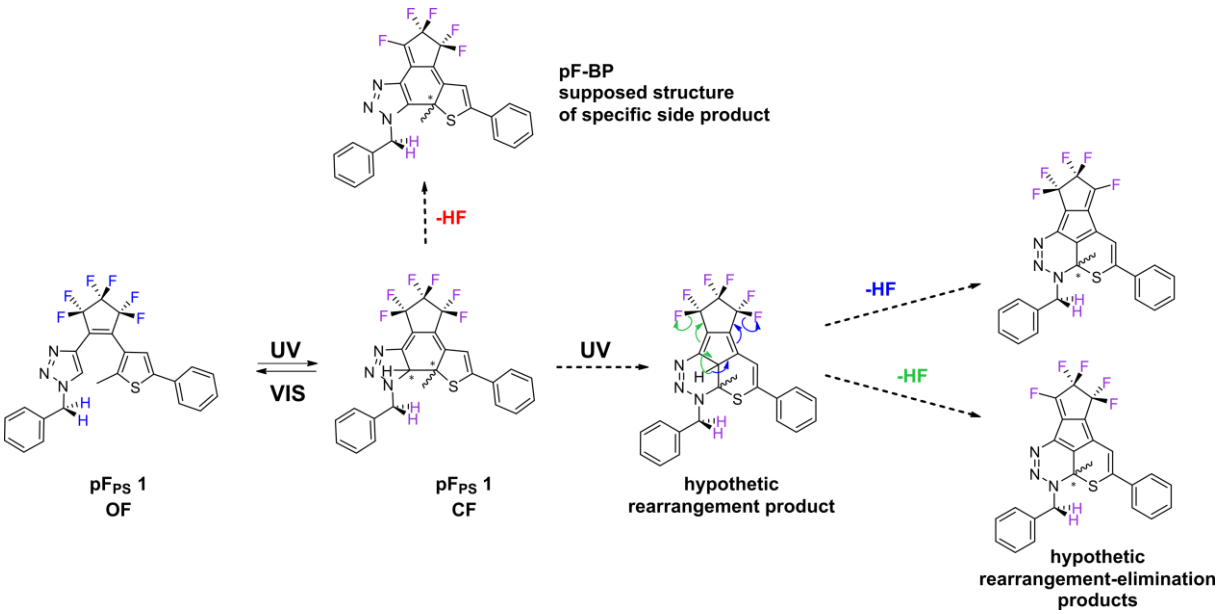


Fig. S7 Structure of **pF$_{PS}$ 1** and HF-elimination from the CF isomer to the assumed most probable structure of the side reaction product during irradiation of **pF$_{PS}$ 1** in methanol (red). A process with a prior rearrangement reaction cannot be excluded (blue, green).

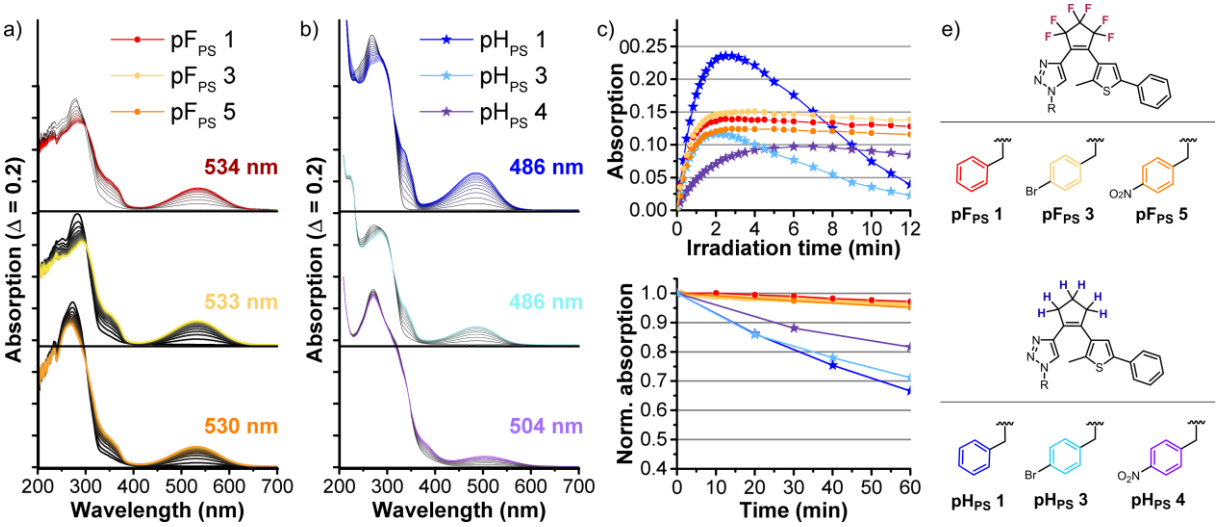


Fig. S8 Influence of substituents on the photochromic properties of perfluoro- and perhydrocyclopentene photoswitches: a) Time-dependent changes in the absorption spectra of **pF$_{PS}$ 1**, **pF$_{PS}$ 3** and **pF$_{PS}$ 5** during irradiation with UV light (310 nm, LED, 60 µM solutions in chloroform), b) Absorption spectra changes of **pH$_{PS}$ 1**, **pH$_{PS}$ 3** and **pF$_{PS}$ 4** during irradiation with UV light (310 nm, LED, 60 µM solutions in methanol), c) Time course of the visible absorption bands during irradiation, d) Thermostability (20 °C), e) Structures of the investigated pF and pH compounds.

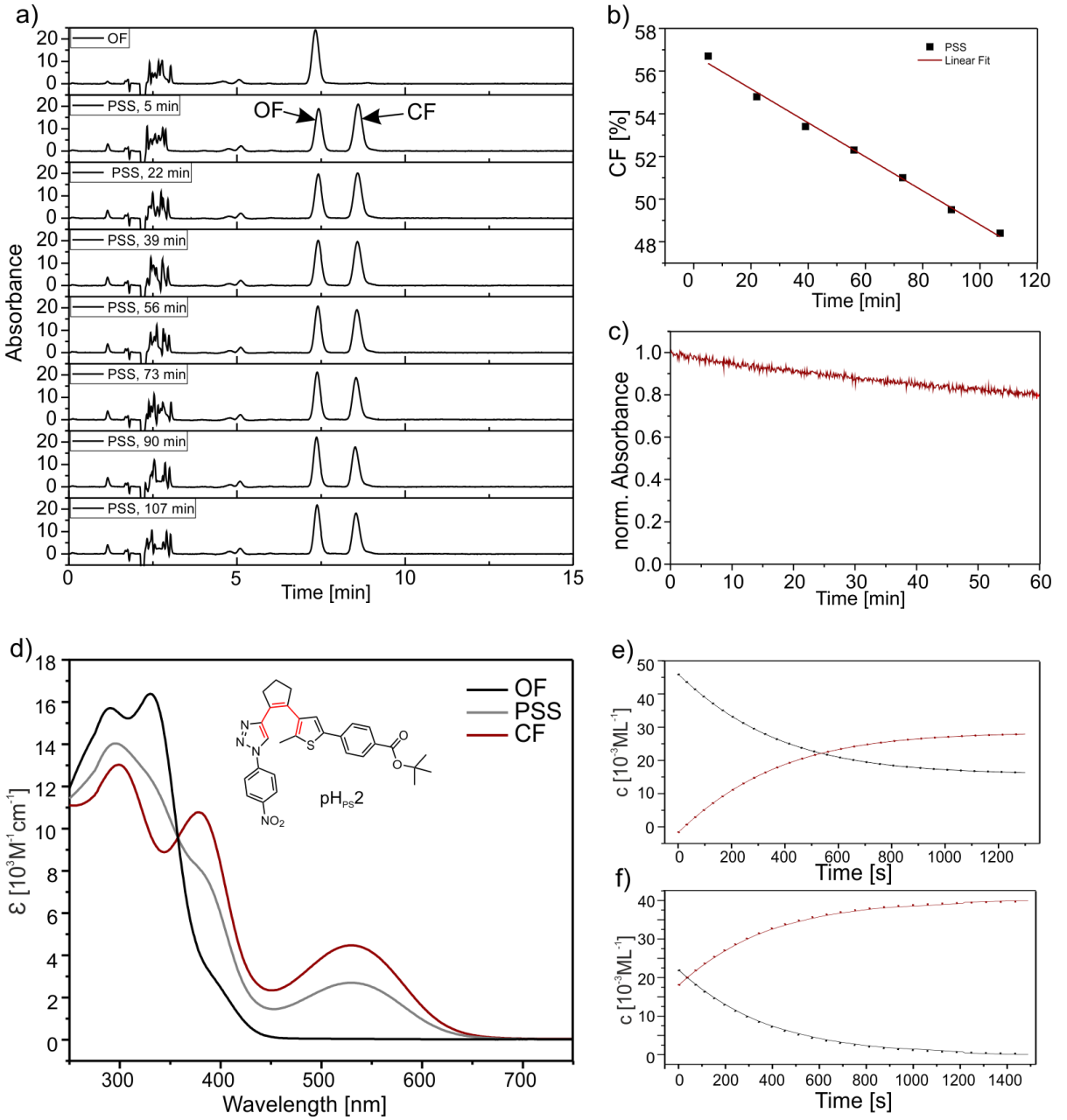


Fig. S9 Determination of (p)PSS composition and reaction quantum yields for **pH$_{PS}$ 2**: a) HPLC analysis for the determination of the PSS. A 60 µM solution of the compound in DMSO was prepared and irradiated with UV light (310 nm LED) until the PSS was reached. Samples containing 50 µL of this mixture were analyzed by HPLC with 358 nm (isosbestic) detection wavelength, whereby the waiting time before HPLC injection was varied between 5 min and 107 min. b) Plot of the % CF, determined from the integrated peak areas in panel a, *vs.* waiting time to extrapolate to t=0 (57% CF). c) Determination of the thermal stability of **pH$_{PS}$ 2** in the HPLC eluent (3:1 acetonitrile/water), indicating that during the HPLC run time, about 2% of CF will decompose, leading to a "true" PSS value of 59±1 % CF. d) Absorption spectra of **pH$_{PS}$ 2**. A 60µM solution in DMSO was prepared and a UV/Vis spectrum was recorded (black line). After the irradiation with UV light (310 nm for 6 min), a UV/Vis spectrum was recorded (gray line). The determined PSS composition (59% CF) was used to calculate the spectrum of the pure closed-ring isomer (red line). e) Time course of the isomer concentrations during the determination of the quantum yield (UV irradiation). A superposition of the calculated concentrations of the two isomers (straight line, red: CF, blue: OF) with the experimentally determined ones (dots) is shown. f) Same analysis for Vis irradiation.

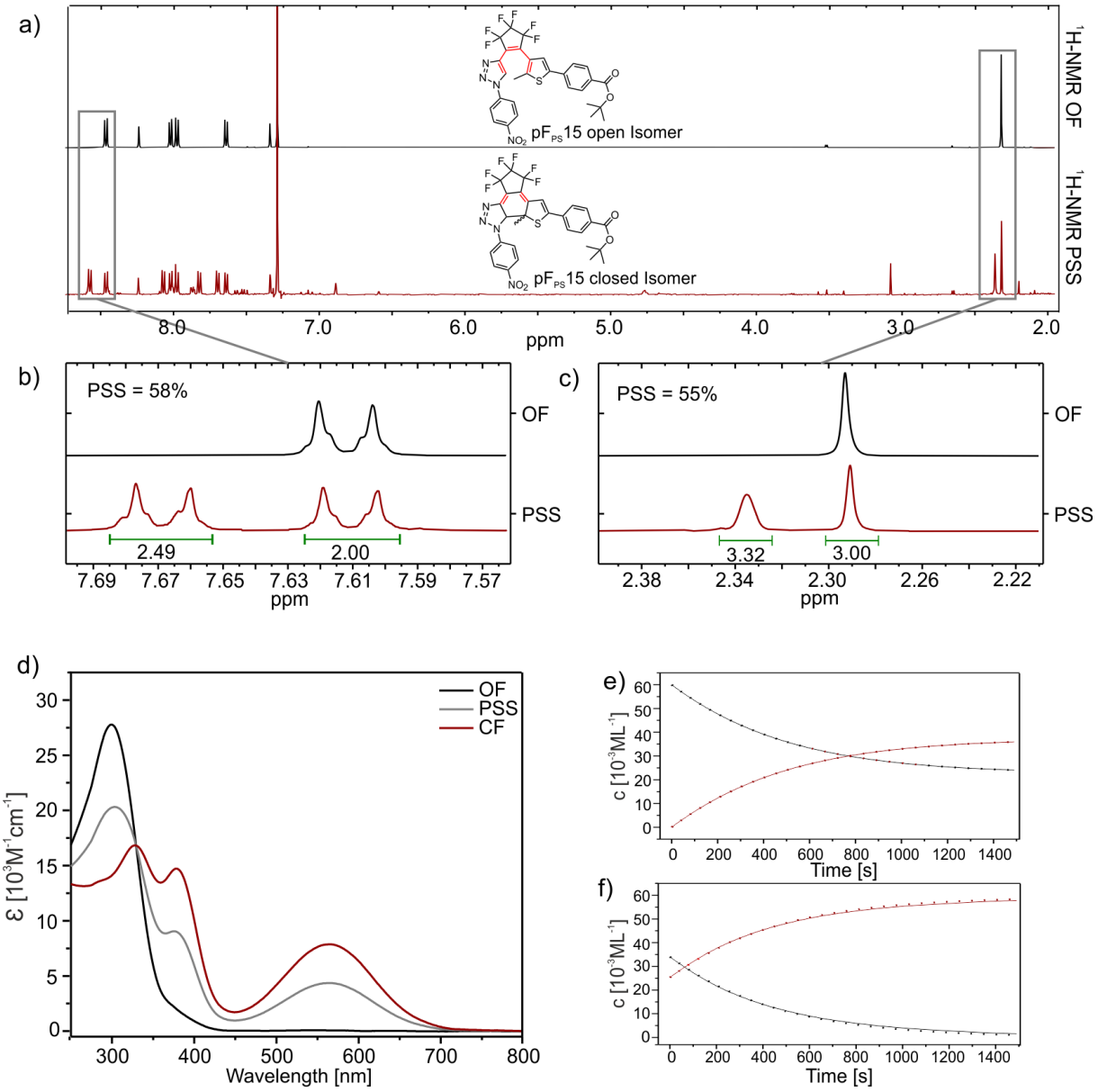
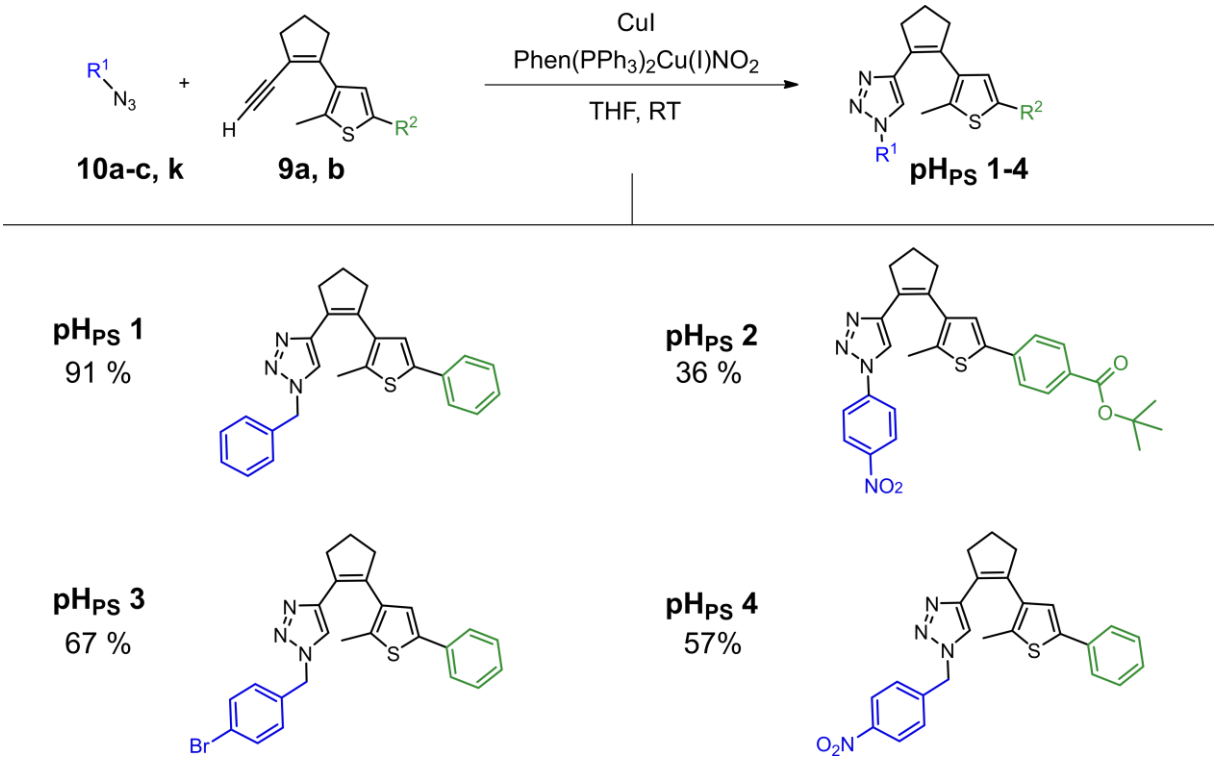


Fig. S10 Determination of (p)PSS composition and reaction quantum yields for **pF$_{PS}$ 15**: a) NMR analysis for the determination of the PSS. The upper panel (black) shows the ^{1}H-NMR of the open isomer of **pF$_{PS}$15**. The PSS was generated by irradiation of a 100 µM solution (3 mL) of the compound in deuterated chloroform. This was repeated five times and the PSS solutions were stored at 0°C under exclusion of light. The combined mixtures were concentrated *in vacuo* and a ^{1}H-NMR was recorded (lower panel, red). b) Zoom into the aromatic region. Integration of the proton signals ortho to the nitro group of open isomer (right) and closed isomer (left) reveals a switching efficiency of 58% (55% +3% thermal decay). c) Zoom into the aliphatic region. Integration of the methyl protons of the open and closed isomers reveals a switching efficiency of 55% (52% +3% thermal decay). d) Absorption spectra of **pF$_{PS}$ 15**. A 40µM solution of the compound in deuterated chloroform was prepared and a UV/Vis spectrum was recorded (black line). After the irradiation with UV light (310 nm for 10 min) another UV/Vis spectrum was recorded (gray line). The determined PSS composition was used to calculate the spectrum of the pure closed-ring isomer (red line). e) Time course of the isomer concentrations during the determination of the quantum yield (UV irradiation). A superposition of the calculated concentrations of the two isomers (straight line, red: CF, blue: OF) with the experimentally determined ones (dots) is shown. f) Same analysis for Vis irradiation.



Scheme S1 Synthesis scheme and yields of the conversion of perhydrocyclopentene acetylenes **9a** and **b** with alkyl azides to perhydrocyclopentene photoswitches **pH$_{PS}$ 1-4**.

Table S1 Absorption spectroscopic data of **pF_{PS} 1-15** (60 µM solutions in chloroform), $\lambda_{UV(OF)}$ absorption maximum of the open isomer, $\lambda_{VIS(CF)}$ visible absorption maximum of closed isomer, $Abs_{(p)PSS}$ maximal VIS absorption ((pseudo)photostationary state), $\varepsilon_{VISmax\ app}$: apparent extinction coefficient at the (p)PSS (at the respective wavelength, calculated by $Abs_{(p)PSS}$/60 µM), Abs_{dec} (%): remaining VIS absorption after 12 min UV irradiation beyond the time the (p)PSS was reached, $\tau_{20\,°C}$ (h): thermal half-life at 20°C.

	$\lambda_{UV(OF)}$ (nm)	$\lambda_{VIS(CF)}$ (nm)	$Abs_{(p)PSS}$	$\varepsilon_{VISmax\ app}$ (*10^4 L/(mol·cm))	Abs_{dec} (%)	$\tau_{20\,°C}$ (h)
pF_{PS} 1	278	534	0.14	0.23	92	16.0
pF_{PS} 2	278	535	0.17	0.28	99	10.9
pF_{PS} 3	284	533	0.15	0.25	92	15.5
pF_{PS} 4	283	534	0.15	0.25	75	3.4
pF_{PS} 5	272	530	0.12	0.20	93	8.8
pF_{PS} 6	282	533	0.11	0.18	94	5.1
pF_{PS} 7	283	531	0.18	0.30	85	5.5
pF_{PS} 8	282	534	0.12	0.20	85	4.2
pF_{PS} 9	283	528	0.24	0.40	97	43.1
pF_{PS} 10	285	558	0.19	0.32	91	4.1
pF_{PS} 11	271	541	0.27	0.45	87	14.0
pF_{PS} 12	290	545	0.28	0.47	77	21.2
pF_{PS} 13	315	536	0.23	0.38	91	7.4
pF_{PS} 14	316	471 und 595	0.11/0.10	0.18/0.17	23/23	1.6
pF_{PS} 15	304	565	0.32	0.53	93	8.4

Table S2 Boltzmann distribution of the four most stable conformers of **pF_{PS} 1 (OF).**

Conformations	-ΔE (KCal/mol)	-ΔE/kT	$e^{-\Delta E/kT}$	% distribution
CH_3 inside phenyl outside	1.078	1.986	7.287	37.25
CH_3 inside phenyl inside	0.000	0.000	1.000	5.11
CH_3 outside phenyl inside	-0.659	-1.214	0.297	1.52
CH_3 outside phenyl outside	1.301	2.396	10.979	56.12

Table S3 Comparison between theoretical and experimental absorption maxima for **pH_{ps} 1.** The calculated values have been obtained at TDDFT/ωB97x-D/cc-pvdz/PCM level of theory.

Solvent	Intermediates	Experimental λmax (nm)	TD-DFT/PCM (nm)	Error (eV)
MeOH	OF	265	276	0.18
	CF	487	440	-0.26
CHCl3	OF	265	275	0.18
	CF	486	442	-0.25

Table S4 Absorption spectroscopic data of pH_{PS} photoswitches (60 µM solutions, different solvents), $\lambda_{UV(OF)}$ Absorption maximum of the open isomer, $\lambda_{VIS(CF)}$ visible absorption maximum of closed isomer, $Abs_{(p)PSS}$ maximal VIS absorption ((pseudo)photostationary state), $\varepsilon_{VISmax\ app}$: apparent extinction coefficient of the closed isomer visible absorption band (at respective wavelength, calculated by $Abs_{(p)PSS}$/60 µM), Abs_{dec} (%): remained VIS absorption after 12 min UV irradiation beyond the time the (p)PSS was reached, $\tau_{20\,°C}$ (h): thermal half-life at 20°C.

	$\lambda_{UV(OF)}$ (nm)	$\lambda_{VIS\,(CF)}$ (nm)	$Abs_{(p)PSS}$	$\varepsilon_{VISmax\ app}$ (*10^4 L/(mol·cm))	Abs_{dec} (%)	$\tau_{20\,°C}$ (h)
pH_{PS} 1 ($CHCl_3$)	273	487	0.17	0.28	05	1.4
pH_{PS} 1 (MeOH)	268	486	0.24	0.40	17	2.0
pH_{PS} 1 (DMSO)	276	486	0.36	0.60	60	2.6
pH_{PS} 2 (DMSO)	332	530	0.22	0.37	96	5.9
pH_{PS} 3 (MeOH)	272	486	0.12	0.20	19	1.6
pH_{PS} 4 (MeOH)	271	504	0.10	0.17	87	2.7

2. Experimental Procedures

2.1. Absorption spectroscopy

Absorption spectroscopic measurements were performed in a Cary 100 UV/VIS spectrometer (Varian/Agilent) equipped with a 6 x 6 Peltier-thermostated multicell-cuvette holder (Series II, Varian, 00-100784-00) and a thermostat (Cary, temperature controller, Varian). 1 ml quartz glass cuvettes were used with a light path of 1 cm. The solvents are listed below:

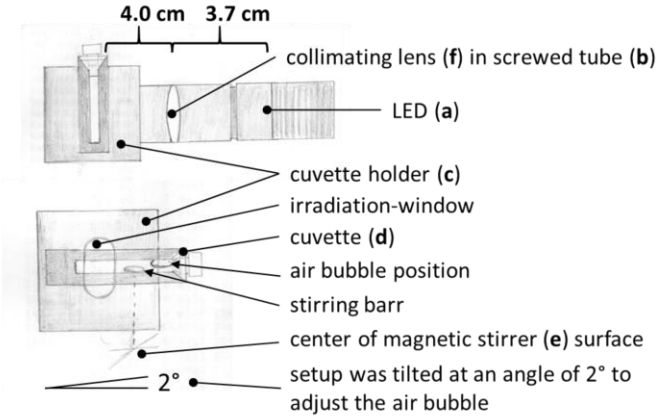
	Source	Specification
Chloroform	Honeywell	Analytical grade
Dichloromethane	Honeywell	Analytical grade
Cyclohexane	Fluka	Analytical reagent grade
Ethylacetate	Zentralbereich Neuenheimer Feld	98-100 %
Dioxane	VWR	Analytical grade
DMSO	Honeywell	Analytical grade, < 0.3 water
Methanol	VWR	≥99.8%, AnalaR NORMAPUR® ACS
Dibromomethane	TCI	>99.0%(GC)

Unless otherwise noted, the measurements were carried out in dual-beam mode at 20 °C, using the solvent as reference in a similar cuvette. Baseline was measured using the solvent in the same cuvette as the sample. The characterization was performed in systems with 1 ml sample volume and 60 ± 0.02 µM solutions. The solutions were prepared by weighing the compound after lyophilization from acetonitrile/water solutions in an Eppendorf tube and successive dissolution in the calculated volume of measuring solvent using Eppendorf pipettes.

2.2. Irradiation method

UV or visible light irradiation of the photoswitches was performed in setups which allow highly reproducible conditions (light intensity, irradiation volume, stirrer position and speed). For UV light irradiation the solutions were stirred using a stirring bar (2mm x 5 mm) placed outside the irradiation volume (see graphic below). 310 nm UV light of a high-power LED from Thorlabs was used, set on maximal intensity (2.10 ± 0.02 mW at the cuvette surface (7.7 ± 0.5 cm to the LED). The light was directed through a collimation lens to reach a higher intensity and consistent irradiation of the solution.

		article number/specification
a	Thorlabs	M310L3 und LEDD1B
b	Thorlabs	SM1L03, SM1L10
c	Thorlabs	CVH100
d	Varian	Cary Quarzglas 7Q
e	IKA	Labdisc
f	Thorlabs	LA4052-UV
g	Thorlabs	S302C (S/N: 150284)



Visible light irradiation was performed in high Intensity mode of an Intralux 6000-1 Fiber Optic Illuminator (VOLPI). The light sources of both fibers were placed in a distance of 4 ± 1 cm to the sample so that the whole solution volume was illuminated and no stirrer was used.

2.3. Characterization of the photochromic properties

Measurements of the **absorption spectra changes** were performed by alternating absorption spectra measurements and UV light irradiation of the sample (chapter 2.2), remaining in the same cuvette during the whole measurement. The irradiation time intervals between the absorption spectra measurements were increased stepwise during the measurements from 10 s to 2 min irradiation duration. 12 min was selected for total irradiation time per sample.

The **photostability curves (kinetic trace)** were determined from these experiments and represent the temporal course of the visible absorption during the UV light irradiation (wavelength is adapted to VIS-absorption maximum of the respective sample, Table S1 and S4). This absorption is proportional to the concentration of the closed form isomers and therefore gives information about the stability of these isomers during the total UV light irradiation time. The determined values were connected with lines only for the sake of clarity (no fitting of the reaction kinetics).

Reversibility measurements were performed by alternate absorption spectra measurement and irradiation, while additionally alternating the irradiation between UV (310 nm) and VIS (lamp spectrum) light (chapter 2.2). During the irradiation processes the measurement solutions remained in the same cuvette that was used for recording the absorption spectra. With regard to the low photostability, the durations of UV light irradiation were selected for optimised reversibility of the respective sample (**pF$_{PS}$ 1** in chloroform: 127 s, **pH$_{PS}$ 1** in DMSO: 2.25 min, **pH$_{PS}$ 2** in DMSO: 5 min).

Visible light irradiation duration was selected for each sample to reach the original absorption value (wavelength of the VIS absorption maximum) of the open form isomer (30-45 s). The irradiation durations of UV and VIS light were kept constant during the experiment of one sample.

Thermostability-measurements were performed in the same absorption spectrometer using the software "Kinetics". The measurement solution was irradiated to the (p)PSS and then the absorption of the VIS band of the closed form was measured in different intervals while the solution was kept in the dark. The measured values were connected with lines only for the sake of clarity (no fitting of the reaction kinetics). The noted values of thermostability (%) refer to the VIS absorption after 60 min at 20 °C relative to the (p)PSS value. Calculated thermostability half-lifes τ were determined from linear or exponential fits.

2.4. HPLC analysis

Analytical HPLC experiments were performed on an Agilent HP 1100 series system. Detection was accomplished by a diode array detector (DAD). Column as well as solvent and other parameters are described separately for the respective experiments in the following. Measurement and data acquisition were performed using the ChemStation software. OriginPro 2015 was used for data analysis.

Solutions of **pF$_{PS}$ 1** and **pH$_{PS}$ 1** were prepared and irradiated the same way as in absorption spectra measurements (60 µM, 1 mL, 310 nm LED irradiation, see chapter 2.1.) in a 1 mL cell. Absorption

spectra were recorded before and after the corresponding irradiation times (see Fig. S5). Chromatograms were measured after each irradiation from the same sample.
HPLC sample injection: 80 µL.
Mobile Phase: Millipore-water (20%), acetonitrile (80%).
Column: Synergi 4u Fusion-RP 80A 250 x 4.6 nm, 4 micron, H18-127089, 5415-0063, 25 °C

2.5. Determination of photostationary state composition and quantum yields

2.5.1 Quantification of the (p)PSS by HPLC

HPLC determination of the (p)PSS could only be applied to the switches of the pH_{PS} series, as the pF_{PS} switches do not tolerate even small amounts of non-halogenated solvents. Attempts to use pure halogenated solvents as HPLC eluents resulted in broad, hardly resolved peaks not suitable for quantification. Another parameter that must be considered is the thermal stability of the CF over the time of the analysis, not only in the solvent used for irradiation, but also in the HPLC eluent. Gradient elution was avoided, as not only the stability, but also the extinction coefficient of the CF may be solvent-dependent.

Method: For the determination of the switching efficiency a 60 µM solution of the compound in DMSO was prepared and irradiated with UV light (310 nm LED: Thorlabs, Mounted High Power LED, operated at 350mA) until the PSS was reached. Samples containing 50 µL of this mixture were analyzed by HPLC measurements, using an Agilent 1100 Series HPLC system equipped with diode array detector (DAD). A Polar-RP 80A (150x4.6mm) column from Phenomenex was used with a flow rate of 1.5 mL/min and eluting with 75% acetonitrile. The absorbance was recorded at the isosbestic wavelength of the open and closed isomers of the photoswitch. The switching efficiency was then determined by calculating the ratio of the peak areas of the open and closed isomer at the isosbestic point.

2.5.2 Quantification of the (p)PSS by NMR spectroscopy

For the above-described reasons, pF_{PS} photoswitches could only be analyzed by NMR spectroscopy. Here, the main difficulty was the concentration required for NMR spectroscopy, which is at least 2 orders of magnitude higher than the concentrations used in our irradiation experiments. Due to inner filter effects and problems arising from the low photostablity of several pF_{PS} compounds, photoswitch concentrations during irradiation could not be significantly increased. However, compounds with high thermal stability could first be irratiated under dilute conditions in a large volume of $CDCl_3$ until the PSS was reached, and then quickly concentrated *in vacuo* and under cooling to NMR concentrations.

Method: NMR-spectra were recorded on a 500 MHz Varian instrument. The PSS was generated by irradiation of a 100 µM solution (3 mL) of the compound in deuterated chloroform. This was repeated five times and the PSS solutions were stored at 0°C under exclusion of light. The combined mixtures were concentrated and a ^{1}H-NMR was recorded.

2.5.3 Quantum yield determination

Quantum yields were measured on an updated Quantum yield determination setup (QYDS) by Megerle *et al.*[1]. Irradiation of the photoswitches was performed, using UV-light LEDs (Nikkiso SMD mounted 300 nm LED, model: VPC173, Dowa SMD mounted 325 nm LED, model: DOWA EOLS-325-696 325_nm (326_nm)) and visible light LED (Osram Oslon SSL80 505nm LED, model: LVCK7P-JYKZ, Luxeon 567 nm LED model: SN115, SP01L1). The LED output radiant power was calibrated against the output voltage

of the solar cell by using a power meter from Coherent (model: PowerMax-USB PS19Q). The raw data measured with the QYDS was further processed with a Mathcad script provided by the E. Riedle group (LMU Munich).

2.6. Syntheses

2.6.1. General

Chemicals were obtained from Sigma-Aldrich, Acros, ChemPur, Carbolution, TCI or abcr and used without further purification. Solvents (cyclohexane, acetonitrile, DCM, chloroform were obtained from Honeywell, later Fischer Scientific) and used without further purification. Dry solvents were purchased under argon atmosphere and used without further drying but were degassed by either flushing with argon or the "freeze-thaw" technique. If not noted differently, distilled water was used.
Reactions with air and/or moisture-sensitive substances were carried out under an argon atmosphere (ALPHAGAZ™ 1 ARGON, ≥ 99,999 mol%, Air Liquide), dry solvents, using Schlenk technique. Solids were added in a protective gas counterflow and subsequent evacuation. Liquids were transferred using septa, steel cannulas and plastic syringes. Lockable Microwave reaction vials (inner diameter of 1.2 cm and a height of 8 cm with a rounded bottom) were flooded with argon under heating and the protective gas counterflow was only switched off immediately before the vessels were closed with aluminum caps (equipped with septum).
Magnetic stirrers were used for mixing. Higher temperatures were automatically maintained in the silicone oil bath using a contact thermometer. Ice baths (0 °C, if necessary, with sodium chloride), ethanol dry ice baths (-78 °C) or ethanol liquid nitrogen baths (up to -100 °C) were used for cooling. Light protection of reactions, columns or substances was ensured with aluminum foil. Volatile substances such as octafluorocyclopentene, trimethylsilylacetylene, tin organyle were injected directly into the pre-cooled solvent to avoid contact with the gas phase. pH values were set and measured with pH paper. For filtration through silica gel (Sigma Aldrich, silica gel 60 M, 0.04 - 0.063 mm) or Celite® 545 (particle size 0.02 - 0.1 mm from Merck), glass frits with a suction bottle were used, the frit was filled 1-3 cm high with silica gel or Celite and after the solution has been filtered, the solid was washed with the respective solvent. Drying of solutions after extraction was carried out by adding the appropriate desiccant (Na_2SO_4 or $MgSO_4$) and subsequent filtration. Unless otherwise noted, solvents were always removed using a rotary evaporator at 40 °C and reduced pressure.

Chromatography:

Reaction control was carried out using thin-layer chromatography plates from Macherey-Nagel (normal phase, POLYGRAM® SIL G / UV254, 40 x 80 mm) or Merk (RP, DC silica gel 60 RP-18 F254s). UV light (254/336 nm) or "blue shift" staining reagent (cerium (IV) sulfate (1 g) and phosphoromolybdic acid (2 g) in 500 mL water and 31 mL concentrated (conc.) Sulfuric acid) were used for this.
Column chromatographic purifications were carried out in glass columns which were packed with silica gel from Sigma Aldrich (60 M, 0.04-0.063 mm) suspended in the respective solvent. Alternatively, purifications were carried out with an IntelliFlash system (Interchim, Puriflash XS series) using reversed phase columns (see details in the method description). The same solvents were used as for the synthesis.
Preparative HPLC purifications were were performed on the same HPLC system mentioned in 2.4. with a preparative column. Samples were dissolved in the initial solvent mixture on a scale between 1 and

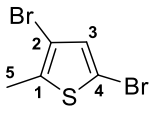
4 mg and injected volumes up to 900 µL. The collected fractions were then always frozen in liquid nitrogen and lyophilized (ALPHA 1-4 LD plus, Christ).

Mobile Phase: gradient of Millipore-water and acetonitrile (20% - 80%).
Column: Luna(R), 5µn C18(2) 100 A, LC Column 250 x 21.2 mm AX, P/No. 006-4252-P0-AX, S/No. H18-025470, B/No 5291-0157 von Phenomenex.

2.6.2. Precursors

The catalyst [1,1'-bis (diphenylphosphino) ferrocene] dichloro-palladium (II) [CAS: 72287-26-4] was used for the Suzuki couplings, which is denoted in the synthesis descriptions as $Pd(dppf)Cl_2$.

3,5-Dibromo-2-methylthiophene **(1)**[2]



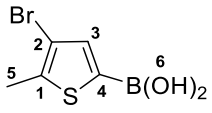
2-Methylthiophene (29.6 mL, 30.0 g, 305 mmol) was dissolved in acetic acid (113 mL) in a 500 ml round bottom flask. The solution was then cooled to 0 °C whereat often crystals were formed in the mixture. A dropping funnel with pressure equalization was attached and then a solution of bromine (36.5 mL, 114 g, 712 mmol) in acetic acid (≥ 99.8%, 46 mL) was added dropwise to the cooled mixture over a period of three hours so that the temperature was kept between 0 and 5 °C. After the addition was complete, the mixture was stirred in an ice bath overnight and allowed to warm up slowly to room temperature.
Water (170 mL) was added slowly and the pH of the mixture was adjusted to 6-7 with Na_2CO_3 powder in an ice bath. After neutralization, the mixture was extracted with diethyl ether (4 × 150 ml). The combined organic phases were dried via $MgSO_4$ and the solvents were removed on a rotary evaporator.
The two-phased mixture was then transferred into a vacuum distillation setup containing a spider. First the remaining acetic acid was distilled off and then the product was obtained at 120 °C and 13 mbar as a clear, colorless oil. 63.8 g (82%).[3]

molecular weight: 255.96 g/mol
chemical formula: $C_5H_4Br_2S$

^{1}H-NMR (300 MHz, CDCl3):
δ (ppm) = 6.85 (s, 1H, H3), 2.34 (s, 3H, H5).

^{13}C-NMR (75 MHz, $CDCl_3$):
δ (ppm) = 136.0, 131.9, 108.8, 108.6, 14.9.

(4-Bromo-5-methylthiophene-2-yl)boronic acid **(2)**[2]



A 500 mL Schlenk flask was evacuated and prepared with dry diethyl ether (200 mL). 3,5-Dibromo-2-methylthiophene **(1)** (13.02 g, 50.87 mmol) was added and the clear solution was cooled to -78 °C. At this temperature, *n*-BuLi solution (2.5 M in hexane, 20.0 mL, 50.0 mmol) was slowly and dropwise added. The yellowish mixture was stirred for 30 min at -78 °C before tributyl borate (14.5 mL, (12.4 g 0.0537 mmol) was added. The mixture was stirred for 1 h at -78 °C and then overnight, while it was allowed to warm up to room temperature. A colorless precipitation could be observed.
The next day, hydrochloric acid (1 M, 200 mL) was added under stirring before the phases were separated. The organic phase was extracted with aqueous NaOH solution (1 M, 3 x 200 mL) and the combined aqueous phases were acidified with conc. HCl, whereby a colorless to yellowish precipitation was formed. Towards the end of the addition (pH 2), the precipitation was cooled in an ice bath. It was filtered off through a suction filter and the brownish solid was dried under high vacuum for about 6 hours in order to obtain the product as an ocher solid. 10.06 g (90%).

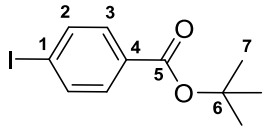
molecular weight: 220.88 g/mol
chemical formula: $C_5H_6BBrO_2S$

^{1}H-NMR (300 MHz, DMSO-*d6*):
δ (ppm) = 8.29 (s, 2H, H6), 7.51 (s, 1H, H3), 2.37 (s, 3H, H5).

^{13}C-NMR (75 MHz, $CDCl_3$):
δ (ppm) = 136.0, 131.9, 108.8, 108.6, 14.9.

tert-Butyl-4-iodobenzoate **(3)**

3 was synthesized in a combined approach from S. Kolodych *et al.* [4] und T. C. Wang *et al.*[5].

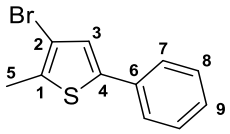


4-Iodobenzoic acid (40 g, 160 mmol) was prepared in an evacuated Schlenk flask and dissolved in thionyl chloride (160 mL). Dry DMF (0.2 mL, 0.19 g, 2.6 µmol) was added and the mixture was then heated under reflux for 1.5 h whereat a clear, yellow solution was formed.
The thionyl chloride was then distilled off under reduced pressure below 50 °C (Liebig cooler, membrane pump, N_2 cooling trap) and the crystallized, colorless solid was dried under high vacuum for 30 min.
The acid chloride was dissolved in dry THF (500 mL) and then potassium *tert*-butoxide powder (22.0 g, 196 mmol) was added slowly and stepwise at room temperature under vigorous stirring. The temperature of the exothermic reaction was controlled by the rate of addition and a water bath and kept below 30 °C.
After the addition was complete (after 1.5 h), the yellow-brown mixture was cooled to 0 °C in an ice bath in order to complete the precipitation. Water and aqueous sat. $NaHCO_3$ solution was added, then the phases were separated and the aqueous phase was extracted three times with DCM. The combined organic phases were pre-dried via Na_2SO_4 and decanted. The mixture was then dried via $MgSO_4$ as usual, filtered and the clear solution was removed using a rotary evaporator. The product was obtained as a yellow, highly viscous and homogeneous oil which crystallized during storage at -20 °C. 34.03 g (70%).

molecular weight: 304.13 g/mol
chemical formula: $C_{11}H_{13}IO_2$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.69 (d, 2H, H3), 7.64 (d, 2H, H2), 1.53 (s, 9H, H7).
^{13}C-NMR (75 MHz, $CDCl_3$):
δ (ppm) = 165.2, 137.6, 131.6, 131.0, 100.1, 81.5, 28.2.

3-Bromo-2-methyl-5-phenylthiophene **(4a)**[6]



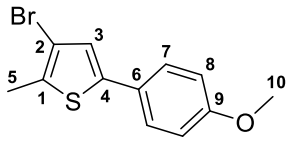
In two 250 ml Schlenk flasks (4-Bromo-5-methylthiophene-2-yl) boronic acid **(2)** (respectively 2,651 g, 12.99 mmol) and the catalyst Pd(dppf)Cl_2 (respectively 439 mg, 0.600 mmol) were prepared. The solid was dissolved in dry THF (respectively 46 mL) and the solution was then degassed using the freeze-thaw technique. Iodobenzene (respectively 1,611 mL, 2,937 g, 14.40 mmol), and aqueous Na_2CO_3 solution (20%, respectively 26.5 mL) were added in protective gas countercurrent and then a Dimroth condenser was attached, which was also flooded with argon. Then the two-phased mixture was refluxed with vigorous stirring overnight at 85 °C.
After cooling to room temperature, the two batches were combined, the phases were separated and the aqueous phase was extracted three times with ethyl acetate. The combined organic phases were washed once with water and then dried via $MgSO_4$. The solvents were removed on a rotary evaporator and the brown oil obtained was purified by column chromatography (silica gel, cyclohexane). The product was obtained as a colorless solid. 4.21 g (69%).

molecular weight: 253,16 g/mol
chemical formula: $C_{11}H_9BrS$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.53-7.48 (m, 2H, H7), 7.40-7.34 (m, 2H, H8), 7.31-7.25 (m, 1H, H9), 7.11 (s, 1H, H3), 2.42 (s, 3H, H5).

^{13}C-NMR (75 MHz, $CDCl_3$):
δ (ppm) = 141.3, 133.8, 133.6, 129.1, 127.9, 125.7, 125.5, 110.0, 15.0.

3-Bromo-5-(4-methoxyphenyl)-2-methylthiophene **(4b)**



(4-Bromo-5-methylthiophene-2-yl) boronic acid **(2)** (2.50 g, 11.3 mmol) and Pd(dppf)Cl_2 (415 mg, 0.567 mmol) were prepared in an evacuated Schlenk flask. Dry THF (44 mL) was added and the solution was degassed by flushing with argon under stirring. 4-Bromoanisole (1.70 mL, 2.54 g, 13.6 mmol) and aqueous Na_2CO_3 solution (20%, 22.1 mL) were added in protective gas countercurrent. Then a Dimroth condenser was attached and flushed with argon before the two-phase mixture was heated at 80 ° C for two days with vigorous stirring.

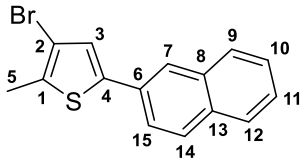
After cooling to room temperature, the phases were separated and the aqueous phase extracted with ethyl acetate (3 x 50 ml). The combined organic phases were washed with water (3 x 40 mL) and then dried via $MgSO_4$ before the solvent was removed on a rotary evaporator. The brown oil obtained was purified by column chromatography (silica gel, gradient: cyclohexane, cyclohexane / ethyl acetate 20:1) and the product was obtained as an orange solid. 1.89 g (59%).

molecular weight: 283.18 g/mol
chemical formula: $C_{12}H_{11}Br_2S$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.46-7.41 (m, 2H, H8), 6.98 (s, 1H, H3), 6.93-6.88 (m, 2H, H7), 3.83 (s, 3H, H10), 2.40 (s, 3H, H5).

^{13}C-NMR (75 MHz, $CDCl_3$):
δ (ppm) = 159.5, 141.2, 132.7, 126.8, 126.5, 124.6, 114.5, 109.8, 55.5, 14.9.

3-Bromo-2-methyl-5-(naphthalene-2-yl)thiophene **(4c)**



(2-Bromo-5-methylthiophene-2-yl)boronic acid **(2)** (respectively 3.00 g, 13.6 mmol) and Pd(dppf)Cl_2 (respectively 500 mg, 0.683 mmol) were prepared in two 250 mL Schlenk flasks. Dry THF (respectively 51 mL) was added and the solution degassed using the freeze-thaw technique. After the last step, the flask was flooded with argon and 2-bromonaphthalene (3.38 g, 16.3 mmol) and aqueous Na_2CO_3 solution (20%, 30 mL) were added in argon countercurrent. A Dimroth cooler was attached and flooded with argon. The two-phase mixture was then refluxed at 80 ° C overnight under vigorous stirring.

After cooling to room temperature, the two batches were combined and the phases were separated from one another. The aqueous phase was extracted with ethyl acetate (4 x 100 mL) and the combined organic phases were washed with water and sat. NaCl solution. It was dried via $MgSO_4$ before the solvent was removed on a rotary evaporator. The brown oil was purified by column chromatography (silica gel, cyclohexane) in order to obtain the product as a colorless solid. 2.88 g (70%).

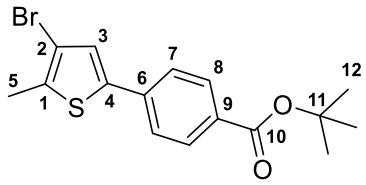
molecular weight: 303.22 g/mol
chemical formula: $C_{15}H_{11}BrS$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.95 (m, 1H, H7), 7.86-7.78 (m, 3H, H9, H12, H14), 7.66-7.61 (m, 1H, H15), 7.53-7.41 (m, 2H, H10, H11), 7.24 (s, 1H, H3), 2.45 (s, 3H, H5).

^{13}C-NMR (75 MHz, $CDCl_3$):

δ (ppm) = 141.3, 134.1, 133.7, 132.9, 131.0, 128.8, 128.2, 127.9, 126.8, 126.3, 126.1, 123.8, 123.8, 110.1, 15.1.

tert-Butyl 4-(4-bromo-5-methylthiophene-2-yl)benzoate **(4d)**



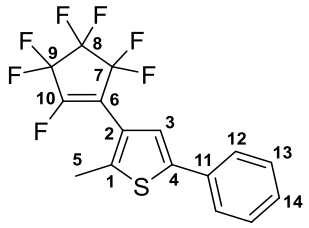
(4-Bromo-5-methylthiophen-2-yl) boronic acid **(2)** (2.89 g, 13.1 mmol) and the catalyst Pd(dppf)Cl_2 (480 mg, 0.656 mmol) were prepared in an evacuated 250 mL Schlenk flask and then dissolved in dry THF (48 mL). The solution was degassed using the freeze-thaw technique and then *tert*-butyl-4-iodobenzoate **(3)** (4.1 g, 13.48 mmol) and aqueous Na_2CO_3 solution (28 mL, 20%$_m$) were added in a protective gas countercurrent. A Dimroth cooler was attached and flooded with argon. Then the two-phased mixture was refluxed under vigorous stirring at 75 °C overnight.
After cooling to room temperature, the phases were separated and the aqueous phase was extracted with ethyl acetate. The combined organic phases were washed with water and then dried via $MgSO_4$. The solvents were removed on a rotary evaporator and the residue was purified by column chromatography (silica gel, gradient: cyclohexane - cyclohexane / ethyl acetate 10:1). The product was obtained as a light-yellow solid. 3.88 g (84%).

molecular weight: 353.27 g/mol
chemical formula: $C_{16}H_{17}BrO_2S$
exact mass 352.01, ESI-MS positive (m/z): 375.0018 (M+Na, calc. 375.0025)

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 8.00-7.94 (m, 2H, H8), 7.56-7.51 (m, 2H, H7), 7.20 (s, 1H, H3), 2.43 (s, 3H, H5), 1.60 (s, 9H, H12).

^{13}C-NMR (75 MHz, $CDCl_3$):
δ (ppm) = 165.4 (C10), 140.1 (C4), 137.3 (C6), 135.3 (C1), 131.1 (C9), 130.3 (C8), 126.9 (C3), 124.9 (C7), 110.4 (C2), 81.3 (C11), 28.4 (C12), 15.1 (C5).

2-Methyl-3-(perfluorcyclopent-1-ene-1-yl)-5-phenylthiophene (**5a**)



Synthesized using a modification of the method reported by Peters[7] and Kobatake[8]. Compound **4a** (3.00 g, 11.9 mmol) was filled into an evacuated Schlenk tube. The solid was dissolved in dry THF (32.9 mL) and the solution was degassed in argon flow under stirring before it was cooled down to -78 °C. *n*-BuLi solution (2.5 M in hexane, 4.80 mL, 12.0 mmol) was slowly added dropwise to prevent the solution from warming up. The solution changed its color several times. After the addition was complete, the mixture was stirred at -78 °C for further 2 h.

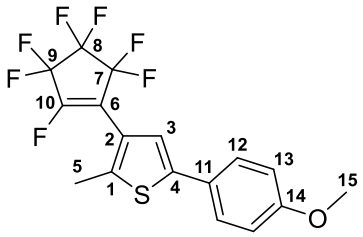
A second Schlenk flask was evacuated and prepared with dry THF (27 mL). The solvent was cooled to -78 °C and then octafluorocyclopentene (2.30 mL, 3.63 g, 17.1 mmol) was dissolved in it.
The solution of the lithium compound was slowly introduced into the perfluorocyclopentene solution via a cannula/septum but without warming up. The mixture was then stirred for further 2 h at -78 °C. Afterwards the mixture was allowed to warm up to room temperature overnight in the cooling bath.
Water (10 mL) was added and the mixture was stirred for few minutes. Then the phases were separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried via $MgSO_4$ and the solvents were removed on a rotary evaporator. A dark brown, highly viscous oil was obtained that was purified by column chromatography (silica gel, cyclohexane). The product was isolated as a light-yellow solid. 3.42 g (79%).

molecular weight: 366,30 g/mol
chemical formula: $C_{16}H_9F_7S$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.58-7.52 (m, 2H, H12), 7.43-7.36 (m, 2H, H13), 7.35-7.28 (m, 1H, H14), 7.25 (s, 1H, H3), 2.50-2.47 (m, 3H, H5).

^{13}C-NMR (75 MHz, $CDCl_3$):
δ (ppm) = 143.2 (C1), 142.7 (C4), 133.3 (C11), 129.2 (C13), 128.2 (C14), 125.9 (C12), 122.3 (C3), 14.9 (C5).

5-(4-Methoxyphenyl)-2-methyl-3-(perfluorcyclopent-1-ene-1-yl)thiophene **(5b)**



Synthesized using a modification of the method reported by Peters[7] and Kobatake[8]. A Schlenk flask was evacuated and compound **4b** (1.62 g, 5.72 mmol) was added. The solid was dissolved in dry THF (25 mL) and the solution was degassed by flushing with argon under stirring. It was cooled to -95 °C and after the temperature had been reached, *n*-BuLi solution (2.5 M in hexane, 3.4 mL, 8.5 mmol) was added slowly and dropwise. During the *n*-BuLi addition the mixture turned turquoise-green. Afterwards the mixture was stirred at -75 °C for 2 h.

A second Schlenk flask was evacuated, dry THF (18.9 mL) was added and the solvent was cooled to -78 °C before the highly volatile octafluorocyclopentene (1.60 mL, 2.53 g, 12.0 mmol) was dissolved in it.

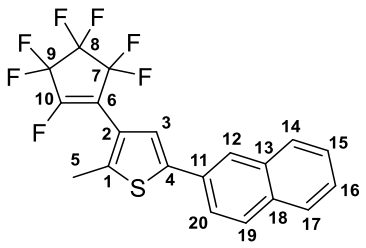
The lithium compound solution was slowly added to the octafluorocylopentene solution at -78 °C while warming of the solution was avoided. Then the mixture was stirred for further 2 h at -78 °C before it was allowed to slowly warm up to room temperature overnight.

Water (20 mL) was added and the phases were separated. The aqueous phase was extracted with diethyl ether (4 x 100 mL) and the combined organic phases were dried via Na_2SO_4. The solvents were removed in vacuo and the obtained brown oil was purified by column chromatography (silica gel, gradient: cyclohexane - cyclohexane/ethyl acetate 20:1). 1.78 g (79 %).

molecular weight: 396.32 g/mol
chemical formula: $C_{17}H_{11}F_7OS$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.48-7.44 (m, 2H, H12), 7.12 (s, 1H, H3), 6.94-6.88 (m, 2H, H13), 3.83 (s, 3H, H15), 2.46 (d, 3H, H5).

2-Methyl-5-(naphthalene-2-yl)-3-(perfluorcyclopent-1-ene-1-yl)thiophene (**5c**)



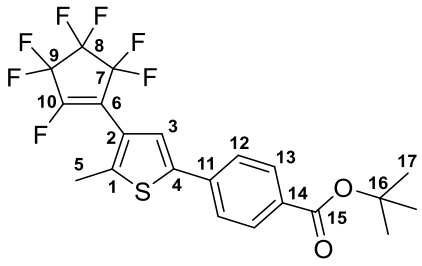
Synthesized using a modification of the method reported by Peters[7] and Kobatake[8]. Compound **4c** (3.00 g, 9.89 mmol) was filled into a 50 mL Schlenk flask and evacuated. The solid was dissolved in dry THF (33 mL) and the solution was degassed in an argon flow under stirring before it was cooled to -78 °C. At this temperature, *n*-BuLi solution (2.5 M in hexane, 3.6 mL, 9.0 mmol) was added slowly and dropwise so that the temperature did not rise significantly. The solution initially turned green. After the addition was complete, the mixture was stirred at -78 °C for 2 h.
Dry THF (27 mL) was prepared in another evacuated 100 mL Schlenk flask and octafluorocyclopentene (2.30 mL, 3.63 g, 17.1 mmol) was dissolved in it. Afterwards the solution was also cooled to -78 °C.

The green solution of the lithium compound was slowly dripped into the octafluorocyclopentene solution, however warming up was avoided. After the addition was complete, the mixture was stirred at -78 °C for 2 h. The mixture was then stirred overnight and the mixture was allowed to warm up to room temperature. Water (20 mL) was carefully added and after a brief stirring the two phases were separated. The aqueous phase was extracted three times with diethyl ether and the combined organic phases were dried over $MgSO_4$. The solvents were removed on a rotary evaporator and a brown oil was obtained, which was purified by column chromatography (silica gel, cyclohexane). The product was obtained as a colorless solid. 1.75 g (43%).

molecular weight: 416.36 g/mol
chemical formula: $C_{20}H_{11}F_7S$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.99-7.98 (m, 1H, H12), 7.89-7.81 (m, 3H, H14,H17,H19), 7.70-7.65 (m, 1H, H20), 7.55-7.45 (m, 2H, H15,H16), 7.37 (s, 1H, H3), 2.52 (d, 3H, H5).

tert-Butyl-4-(5-methyl-4-(perfluorcyclopent-1-ene-1-yl)thiophene-2-yl)benzoate **(5d)**



Synthesized using a modification of the method reported by S. Kobatake, M. Irie[8]. Compound **4d** (1.00 g, 2.83 mmol) was placed in an evacuated Schlenk tube and dissolved in dry THF (17 mL). The solution was degassed using the freeze-thaw technique and then cooled to -105 °C. (ethanol/N_2 bath). After the temperature had been reached, *n*-BuLi solution (2.5 M in hexane, 1.2 mL, 3.0 mmol) was slowly added dropwise over a period of 1 hour, avoiding warming up above -90 °C. During the addition, the color of the solution changed from green to dark blue to yellow-black. After the addition was complete, the mixture was first stirred at -105 °C for a further 10 min, then at -100 °C for 15 min and up to -90 °C for 1 h.

A 50 mL Schlenk flask was evacuated and prepared with dry THF (3.0 mL). Octafluorocyclopentene (0.70 mL, 1.1 g, 5.2 mmol) was added through a septum and the solution was then also cooled to -105 °C.

Both tubes were connected to each other with a metal cannular and the solution of the lithium compound was transferred slowly to the octafluorocyclopentene solution to avoid warming above -90 °C. The mixture initially turned orange and after complete addition it remained brown-red and clear. It was stirred for further 30 min at -90 °C and was then allowed to warm up to room temperature overnight in the cooling bath.

Water (15 mL) was added and stirred for 10 min. The phases were then separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were pre-dried via Na_2SO_4 and decanting and then dried via $MgSO_4$. The crude product was then purified by column chromatography (silica gel, gradient: cyclohexane - cyclohexane / diethyl ether 20:1). The product was isolated as a highly viscous, yellow oil. 0.86 g, 85%$_m$ Product, 0.73 mg (55% yield).

molecular weight: 466.41 g/mol
chemical formula: $C_{21}H_{17}F_7O_2S$
exact mass 466.08, ESI-MS positive (m/z): 489.0726 (M+Na, calc. 489.0730)

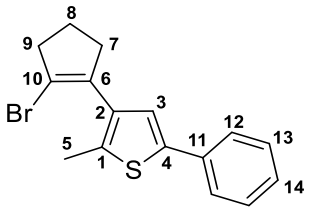
^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 8.02-7.97 (m, 2H, H13), 7.60-7.55 (m, 2H, H12), 7.33 (s, 1H, H3), 2.50 (d, 3H, H5, $^4J_{(H,H)}$ = 2.97 Hz), 1.61 (s, 9H, H17).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 165.4 (C15), 144.3 (C1), 141.6 (C4), 136.9 (C11), 131.6 (C14), 130.4 (C13), 125.4 (C12), 123.6 (C3), 120.9 (C2), 81.4 (C16), 28.4 (C17), 14.9 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -108.3 - -108.5 (m, 2F, F7), -118.0 - -118.2 (m, 2F, F9), -126.9 - -127.2 (m, 1F, F10), -129.9- -130.0 (m, 2F, F8).

The thienyl perhydrocyclopentenes (namely **7a** and **7b**) are literature-known. Dehalogenated thienyl compounds that are formed as by-products are often not completely separable (especially in the case of derivatives with polar groups). The reaction yields are determined by ^{1}H-NMR spectroscopy, if appropriate.

3-(2-Bromocyclopent-1-ene-1-yl)-2-methyl-5-phenylthiophene **(7a)**

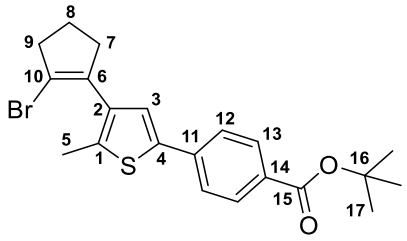


Synthesized analogous to the method described by M. Singer, A. Jäschke.[6] In three 100 mL Schlenk flasks, compound **4a** (2.10 g, 8.30 mmol each) was dissolved in dry THF (52 mL). The solution was degassed by flushing with argon under stirring and then cooled to -78 °C. After reaching the temperature, *n*-BuLi solution (2.5 M in hexane, 4.60 mL, 11.5 mmol) was added slowly to avoid warming. The mixture turned dark blue at first and after a few minutes over dark brown to dark yellow. After the addition was completed, the mixture was stirred at -78 °C for another hour.
Tributyl borate (1.60 mL, 1.37 g, 5.91 mmol) was added and the mixture turned light yellow. The mixture was then stirred at -78 °C for 50 min. It was then allowed to warm slowly to room temperature in about 2 h. Aqueous Na_2CO_3 solution (20 %, 11 mL) and $Pd(dppf)Cl_2$ (348 mg, 0.476 mmol) and dibromocyclopentene (3.5, 6.63 g, 29.36 mmol) were added in argon countercurrent. A Dimroth condenser was placed on top and flooded with argon. Then the two-phase mixture was refluxed at 75 °C overnight under vigorous stirring.
After cooling to room temperature, the phases were separated and the aqueous phase was extracted three times with ethyl acetate. The combined organic phases were washed once with water and then dried over $MgSO_4$. The solvents were removed on a rotary evaporator, combining all three preparations. The brown oil obtained was purified by column chromatography (silica gel, cyclohexane) to give the product as a slightly yellowish and waxy solid. 1.82 g, of which 93.37 $\%_m$ product (next to the typical dehalogenated side product): 1.70 g (64 % yield).

molecular weight: 319.26 g/mol
chemical formula: $C_{16}H_{15}BrS$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.57-7.51 (m, 2H, H12), 7.38-7.31 (m, 2H, H13), 7.26-7.20 (m, 1H, H14), 7.13 (s, 1H, H3), 2.85-2.77 (m, 2H, H9), 2.69-2.60 (m, 2H, H7), 2.42 (s, 3H, H5), 2.12-2.01 (m, 2H, H8).

tert-Butyl-4-(4-(2-bromocyclopent-1-ene-1-yl)-5-methylthiophene-2-yl)benzoate **(7b)**



Compound **4d** (2.00 g, 5.66 mmol) was placed in an evacuated Schlenk flask and the solid was dissolved in dry THF (65 mL). The solution was degassed by flushing with argon under stirring. It was then cooled to -100 to -90 °C. After reaching the temperature, *n*-BuLi solution (2.5 M in hexane, 2.90 mL, 7.25 mmol) was added very slowly to avoid heating the solution above -90 °C (> 30 min for the addition). During the addition the color changed from yellow, light green to turquoise to dark blue. The mixture was further stirred at 100 to -90 °C for 1 h after complete addition and turned deep red.
Tributyl borate (2.64 mL, 2.44 g, 23.4 mmol) was added slowly to avoid warming. The mixture was then allowed to warm up slowly in a cooling bath to -70 °C within 1 h. Within two more hours, the mixture was allowed to warm up slowly to room temperature by removing the cooling bath after 1 h and using a water bath at the end.
The clear red solution was degassed again by flushing with argon under stirring and then the catalyst $Pd(dppf)Cl_2$ (250 mg, 0.342 mmol), 1,2-dibromocyclopentene (1.10 mL, 2.09 g, 9.23 mmol) and aqueous Na_2CO_3 solution (20 %, 20 mL) were added in the inert gas flow (similar conditions used for the synthesis of **7a**). A Dimroth cooler was placed and flooded with argon. The two-phase mixture was then refluxed at 75 °C overnight under vigorous stirring.
After cooling to room temperature, the phases were separated and the aqueous phase was extracted with ethyl acetate. The combined organic phases were dried over $MgSO_4$, filtered through a layer of silica (4.5 cm height, 3.5 cm Ø) and the silica layer was washed with ethyl acetate. The solvents were removed on a rotary evaporator and the brown oil obtained was purified by column chromatography (silica gel, gradient: cyclohexane - cyclohexane/diethyl ether 200:3). The product was obtained as a violet oil. 1.40 g, of which 73 $\%_m$ product: 1.04 g (44 % yield).

After column chromatography, dehalogenated phenylthiophene was still detected. For the next reaction steps **6d** was used without additional purification, since the impurities were not expected to react in the further synthesis step and could easily be removed after the conversion to the photoswitch.

molecular weight: 419.28 g/mol
chemical formula: $C_{21}H_{23}BrO_2S$
exact mass 418.06, ESI-MS positive (m/z): 441.0486 (M+Na, calc. 441.0494)

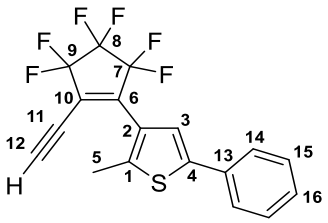
^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.98-7.93 (m, 2H, H13), 7.59-7.55 (m, 2H, H12), 7.22 (s, 1H, H3), 2.84-2.79 (m, 2H, H9), 2.68-2.63 (m, 2H, H7), 2.44 (s, 3H, H5), 2.13-2.05 (m, 2H, H8), 1.60 (s, 9H, H17).

^{13}C-NMR (125 MHz, $CDCl_3$):

δ (ppm) = 165.6 (C15), 139.0 (C11), 138.3 (C14), 137.1 (C1), 136.4 (C10), 135.0 (C2), 130.2 (C13), 125.0 (C4), 125.0 (C3), 125.0 (C12), 119.4 (C6), 81.1 (C16), 41.1 (C9), 37.0 (C7), 28.4 (C17), 22.6 (C8), 15.2 (C5).

2.6.3. Cyclopentene acetylenes

3-(2-Ethynyl-3,3,4,4,5,5-hexafluorcyclopent-1-ene-1-yl)-2-methyl-5-phenylthiophene **(6a)**



Three lockable microwave vials were prepared with dry THF (respectively 3.1 mL). The solvent was degassed by flushing with argon under stirring and was then cooled to -78 °C. Trimethylsilylacetylene (respectively 0.262 g, 2.67 mmol) was dissolved and *n*-butyllithium (2.5 M in hexane, respectively 1.1 mL, 2.75 mmol) was added slowly at -78 °C to avoid warming. The clear colorless solution was stirred for 2 h at -78 °C and thereafter 30 min at 0 °C (ice bath) to complete the reaction. At the end it was cooled down to -78 °C again.
Compound **5a** (465 mg, 1.27 mmol each) was dissolved in dry THF (1.5 mL) in three lockable microwave vials and degassed by argon flow under stirring. This solution was then slowly added dropwise to the acetylene solution at -78 °C. After the addition was complete, the mixture was stirred at -78 °C for 1.5 h and then at 0 °C for 30 min, during which the mixture turned dark red. The mixture was then stirred at room temperature for 30 min (water bath), during which the solution turned brown. Water was added and the phases were separated. The aqueous phase was extracted three times with diethyl ether and the combined organic phases were washed once with water before drying over $MgSO_4$. The solvents were removed on a rotary evaporator and the brown oil obtained was then purified by column chromatography (silica gel, cyclohexane). The product was obtained as a highly viscous, brownish oil which slowly crystallized in needles during storage at -20 °C. 1.08 g (76%).

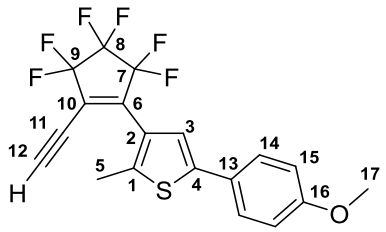
molecular weight: 372,33 g/mol
chemical formula: $C_{18}H_{10}F_6S$
exact mass 372.04, HR-EI-MS (m/z): 372.0391 (M+H, calc. 372.0402)

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.58-7.53 (m, 2H, H12), 7.43-7.35 (m, 2H, H13), 7.34-7.27 (m, s, 2H, H3, H14), 3.68 (s, 1H, H12), 2.52 (s, 3H, H5).

^{13}C-NMR (75 MHz, $CDCl_3$):
δ (ppm) = 143.8 (C1), 142.3 (C4), 133.3 (C13), 129.2 (C15), 128.2 (C16), 125.9 (C14), 124.9 (C2), 122.5 (C3), 116.0 (tvtvt, C7/C9), 114.7 (tvtvt, C7/C9), 111.0 (tvtvt, C8), 92.5 (C11), 72.6 (C12), 15.8 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.5 - -110.6 (m, 2F, F7/F9), -111.2- -111.3 (m, 2F, F7/F9), -131.8 - -132.0 (m, 2F, F8).

3-(2-Ethynyl-3,3,4,4,5,5-hexafluorcyclopent-1-ene-1-yl)-5-(4-methoxyphenyl)-2-methylthiophene **(6b)**



Dry THF (respectively 2.33 mL) was placed in three evacuated microwave vials and the solvent was degassed by flushing with argon under stirring. After cooling to -80 °C trimethylsilylacetylene (respectively 0.53 mL, 0.38 g, 3.8 mmol) was dissolved. The mixture was stirred for 5 min before *n*-BuLi solution (2.5 M in hexane, respectively 1.02 mL, 2.55 mmol) was slowly and dropwise added to prevent the mixture from warming up. After the addition was complete, the mixture was stirred at -78 °C for 1 h, then in an ice bath for 30 min at 0 °C and finally it was cooled again to -78 °C.
A solution of compound **5b** (respectively 0.660 g, 1.66 mmol) in dry THF (0.5 mL) was slowly and dropwise added at -78 °C and the mixture was then stirred at -78 °C for 1 h. Afterwards it was stirred in an ice bath at 0 °C for 30 min and at the end in a water bath for 30 min at room temperature.
Water (respectively 1 mL) was added and the batches were combined. The phases were separated and the aqueous phases were extracted with diethyl ether. The combined organic phases were dried via $MgSO_4$ and the solvents were removed on a rotary evaporator to obtain a brown oil. The product was isolated by column chromatography (silica gel, gradient: cyclohexane - cyclohexane / ethyl acetate 50:1) and obtained as a brownish solid. 1.03 g (52%).

After column chromatography, minor impurities were still detected. NMR analysis was performed on a HPLC purified sample. For the next reaction steps **6b** was used without additional purification, since the impurities (primarily para-bromo-anisole) did not interfere with the further synthesis and could easily be removed after the conversion to the photoswitch.

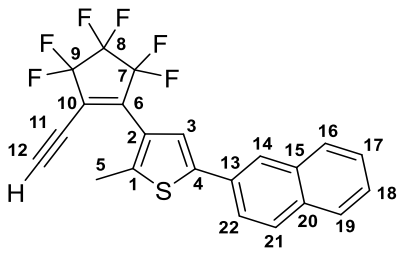
molecular weight: 402.35 g/mol
chemical formula: $C_{19}H_{12}F_6OS$
exact mass 402.05, HR-EI-MS (m/z): 402.0518 (M+H, calc. 402.0508)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.50-7.45 (m, 2H, H15), 7.19 (s, 1H, H3), 6.94-6.89 (m, 2H, H14), 3.84 (s, 3H, H17), 3.67 (s, 1H, H12), 2.50 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 159.7 (C16), 142.9 (C1), 142.2 (C13), 127.2 (C15), 126.2 (C4), 124.8 (C2), 121.4 (C3), 114.6 (C14), 92.4 (C12), 72.7 (C11), 55.5 (C17), 15.8 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.5 - -110.6 (m, 2F, F7/F9), -111.2 - -111.3 (m, 2F, F7/F9), -131.8 - -131.9 (m, 2F, F8).

3-(2-Ethynyl-3,3,4,4,5,5-hexafluorcyclopent-1-ene-1-yl)-2-methyl-5-(naphthalene-2-yl)thiophene **(6c)**



Dry THF (3.5 ml) was placed in a lockable microwave vial and the solvent was degassed by stirring under argon flow. The vessel was closed and the solution was cooled to -78 °C Trimethylsilylacetylene (0.50 ml, 0.36 g, 3.6 mmol) was dissolved and after 5 min, *n*-BuLi solution (2.5 M in hexane, 1.41 ml, 3.53 mmol) was slowly added dropwise, so that warming up of the mixture was avoided. After the addition was complete, the mixture was stirred for 2 h at -78 °C and then for 30 min in an ice bath (0 °C). Before the next step it was then cooled again to -78 °C.
At this temperature, a solution of compound **5c** (0.850 g, 2.04 mmol) in dry THF (2.8 ml, degassed by flushing with argon) was slowly added dropwise, and the mixture was then stirred at -78 °C for 1.5 h, whereat it turned brown. The mixture was then stirred in an ice bath for 30 min and successively in a water bath at room temperature for a further 30 min.
Water (4 mL) was added to the black-yellow solution and the phases were separated. The aqueous phase was extracted with diethyl ether (3 x 30 mL) and the combined organic phases were washed once with water (25 mL) and then dried over $MgSO_4$. The solvents were removed on a rotary evaporator, giving a brown oil. The crude product was then purified by column chromatography (silica gel, cyclohexane) and the product was obtained as a yellow solid. 0.67 g (77 %).

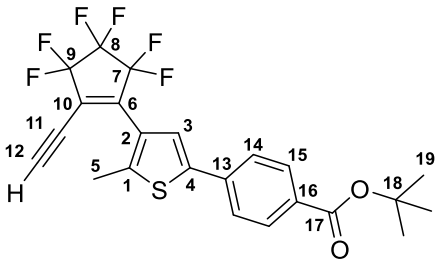
molecular weight: 422.39 g/mol
chemical formula: $C_{22}H_{12}F_6S$
exact mass 422.06, HR-EI-MS (m/z): 422.0552 (M+H, calc. 422.0558)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 8.00-7.98 (m, 1H, H14), 7.88-7.81 (m, 3H, H16,H19,H21), 7.70-7.66 (m, 1H, H22), 7.53-7.45 (m, 2H, H17,H18), 7.44 (s, 1H, H3), 3.70 (s, 1H, H12), 2.55 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 144.0 (C1), 142.3 (C4), 133.7 (C15), 133.1 (C20), 130.7 (C13), 128.9 (C21), 128.2 (C16), 127.9 (C19), 126.9 (C17/C18), 126.5 (C17/C18), 125.0 (C2), 124.5 (C14), 124.0 (C22), 122.9 (C3), 118.0-108.9 (C6,C7,C8,C9,C10), 92.5 (C12), 72.6 (C11), 15.9 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.5 - -110.6 (m, 2F, F7/F9), -111.2 - -111.3 (m, 2F, F7/F9), -131.8 - -131.9 (m, 2F, F8).

tert-Butyl-4-(4-(2-ethynyl-3,3,4,4,5,5-hexafluorcyclopent-1-ene-1-yl)-5-methylthiophene-2-yl)benzoate **(6d)**



Dry THF (3.7 mL) was placed in a lockable microwave vial and degassed by flushing with argon under stirring. Then the vessel was closed and the solvent cooled to -80 °C (EtOH/N_2). Trimethylsilylacetylene (respectively 430 µL, 0.310 g, 3.10 mmol) was dissolved and after stirring for 5 min, *n*-BuLi solution (2.5 M in hexane, 1.3 mL, 3.3 mmol) was slowly and dropwise added. After the addition was complete, the mixture was stirred at -80 °C for 2 h and then for 30 min at 0 °C (ice bath) before it was cooled to -90 °C. In a second, evacuated microwave vial, compound **5d** (900 mg, 1.93 mmol) was dissolved in dry THF (2.9 mL), the solution was degassed by stirring with argon and then also cooled to -90 °C. At this temperature, it was then added slowly and dropwise to dissolve the lithium compound. The mixture first turned green and then dark brown. After the addition was complete, the mixture was stirred at -90 °C for 1 h and then allowed to warm up to -80 °C and stirred again for 30 min.
The cooling bath was removed and water (4 mL) was added directly to the mixture before it was allowed to warm up further to room temperature. A slight gas formation could be observed. The phases were separated and the aqueous phase was extracted three times with diethyl ether. The combined organic phases were dried via $MgSO_4$ and the solvents were removed on a rotary evaporator. The crude product was purified by column chromatography (silica gel, gradient: cyclohexane - cyclohexane / ethyl acetate 20:1). The product was obtained as a yellow oil. 1,017 g, 56 $\%_m$ Product, 570 mg (63% yield).

After column chromatography, dehalogenated phenylthiophene and **5d** were still detected. NMR analysis was performed on a HPLC purified sample. For the next reaction steps **6d** was used without additional purification, since the impurities were not expected to react in the further syntheses and could easily be removed after the conversion to the photoswitch.

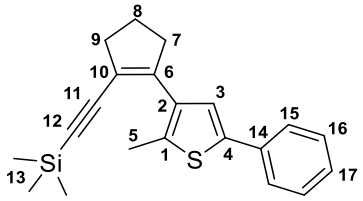
molecular weight: 472.45 g/mol
chemical formula: $C_{23}H_{18}F_6O_2S$
exact mass 472.09, ESI-MS positive (m/z): 495.0807 (M+Na, calc. 495.0824)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.97-7.94 (m, 2H, H15), 7.58-7.56 (m, 2H, H14), 7.39 (s, 1H, H3), 3.69 (s, 1H, H12), 2.53 (s, 3H, H5), 1.61 (s, 9H, H9).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 165.7 (C17), 144.8 (C1), 141.1 (C4), 138.6 (C13), 131.4 (C16), 130.2 (C15), 125.1 (C2), 125.0 (C14), 123.7 (C3), 92.7 (C12), 81.4 (C18), 72.5 (C11), 28.4 (C19), 15.8 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.5 - -110.6 (m, 2F, F7/F9), -111.3 (m, 2F, F7/F9), -131.8 - -131.9 (m, 2F, F8).

Trimethyl((2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)ethynyl)silane **(8a)**



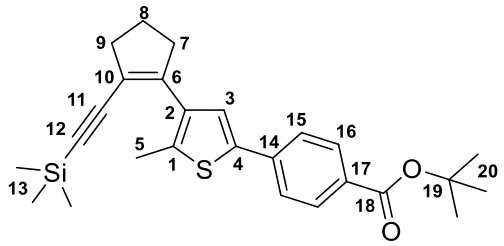
Compound **7a** (152 mg, 0.480 mmol) was placed in a closable microwave vial, the vessel was closed and evacuated. The solid was dissolved in dry toluene (5 mL) and the solution was then degassed with argon while stirring.
$Pd(PPh_3)_2Cl_2$ (20 mg, 0.030 mmol) was added and the vessel was closed again. Trimethyl [(tributylstannyl)ethynyl]silane (0.21 mL, 222 mg, 0.57 mmol) was added dropwise with stirring at room temperature. After the addition was complete, the cloudy, yellow mixture was heated to 100 °C and then stirred at this temperature overnight.
After cooling to room temperature, the solvent was removed on a rotary evaporator and the residue was purified by column chromatography (silica gel, cyclohexane). The product was obtained as a yellow solid. 118 mg (74%).

molecular weight: 336.57 g/mol
chemical formula: $C_{21}H_{24}SSi$
exact mass 336.14, HR-EI-MS (m/z): 336.1362 (M+H, calc. 336.1362)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.58-7.53 (m, 2H, H15), 7.51 (s, 1H, H3), 7.38-7.32 (m, 2H, H16), 7.26-7.22 (m, 1H, H17), 2.84-2.77 (m, 2H, H9), 2.70-2.63 (m, 2H, H7), 2.50 (s, 3H, H5), 2.03-1.94 (m, 2H, H8), 0.18 (s, 9H, H13).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 145.5 (C6), 139.2 (C4), 136.3 (C1), 135.2 (C2), 134.6 (C14), 128.9 (C16), 127.1 (C17), 125.5 (C15), 124.3 (C3), 120.1 (C10), 103.7 (C11), 99.9 (C12), 37.9 (C7), 37.7 (C9), 23.5 (C8), 15.9 (C5), 0.21 (C13).

tert-Butyl-4-(5-methyl-4-(2-((trimethylsilyl)ethynyl)cyclopent-1-ene-1-yl)thiophene-2-yl)benzoate **(8b)**



Compound **7b** (1.46 g, 2.50 mmol) was prepared in an evacuated Schlenk flask and dissolved in dry toluene (25 mL). The solution was degassed by flushing with argon under stirring and then the catalyst $Pd(PPh_3)_2Cl_2$ (77 mg, 0.11 mmol) was added in countercurrent gas and trimethyl[(tributylstannyl)ethynyl]silane (0.85 mL, 898.6 mg, 2,319 mmol) was added. A Dimroth cooler was attached and flooded with argon before the mixture was heated to 100 °C and stirred overnight.

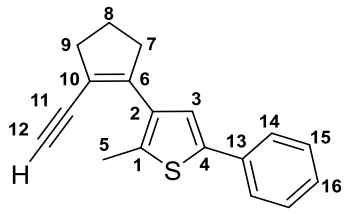
After the dark colored mixture was cooled to room temperature, the mixture was filtered through a layer of silica gel (4.5 cm high, 3.5 cm Ø) and washed with ethyl acetate. The solvents were then removed on a rotary evaporator and the residue was purified by column chromatography (silica gel, gradient: cyclohexane, cyclohexane / diethyl ether 200:1). The product was obtained as a bright solid which still contained significant amounts of the dehalogenated thiophene. 1,461 g, of which 68.85% m product: 1.01 g (92%).

molecular weight: 436.69 g/mol
chemical formula: $C_{26}H_{23}O_2SSi$
exact mass 436.19, ESI-MS positive (m/z): 459.1783 (M+Na, calc.459.1784)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.98-7.95 (m, 2H, H16), 7.62 (s, 1H, H3), 7.59-7.55 (m, 2H, H15), 2.82-2.76 (m, 2H, H9), 2.69-2.63 (m, 2H, H7), 2.50 (s, 3H, H5), 2.01-1.94 (m, 2H, H8), 1.61 (s, 9H, H20), 0.18 (s, 9H, H13).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 165.6 (C18), 145.0 (C6), 141.1 (C4), 138.3 (C17), 138.0 (C14), 137.6 (C1), 135.5 (C2), 130.1 (C16), 125.6 (C3), 124.9 (C15), 120.5 (C10), 103.5 (C11), 100.0 (C12), 81.0 (C19), 37.9 (C6), 37.6 (C10), 28.3 (C20), 15.9 (C5), 0.16 (C13).

3-(2-Ethynylcyclopent-1-ene-1-yl)-2-methyl-5-phenylthiophene **(9a)**



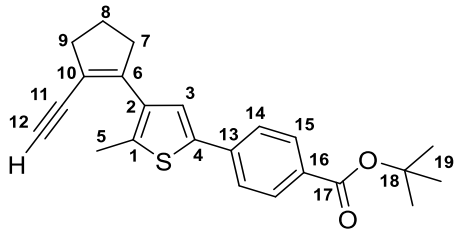
Compound **8a** (260 mg, 0.770 mmol) was placed in a closed microwave vial, the vessel was evacuated and the solid was dissolved in dry THF (17 mL). The yellow solution was briefly degassed by flushing with argon under stirring before it was cooled to 0 °C. TBAF solution (1M in THF, 1.0 mL, 1.0 mmol) was slowly and dropwise added at this temperature. Afterwards the mixture was stirred at 0 ° C for 1 h before the ice bath was removed and the mixture was stirred at room temperature for additional 6 h. The solvent was then removed in vacuo and the residue was purified by column chromatography (silica gel, cyclohexane). The product was isolated as a brown, glassy oil. 130 mg (64%).

molecular weight: 264.39 g/mol
chemical formula: $C_{18}H_{16}S$
exact mass 264.10, ESI-MS positive (m/z): 265.1043 (M+H, calc. 265.1045)
287.0875 (M+Na, calc. 287.0865)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.56-7.52 (m, 2H, H14), 7.38-7.33 (2H, H15), 7.37 (s, 1H, H3), 7.26-7.22 (m, 1H, H16), 3.18 (s, 1H, H12), 2.82-2.77 (m, 2H, H9), 2.71-2.66 (m, 2H, H7), 2.49 (s, 3H, H5), 2.05-1.97 (m, 2H, H8).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 146.0 (C6), 139.7 (C4), 136.3 (C1), 135.0 (C2), 134.6 (C13), 128.9 (C15), 127.2 (C16), 125.6 (C14), 124.0 (C3), 119.4 (C10), 82.3 (C12), 82.0 (C11), 37.9 (C7,C9), 23.3 (C8), 15.7 (C5).

tert-Butyl-4-(4-(2-ethynylcyclopent-1-en-1-yl)-5-methylthiophene-2-yl)benzoate **(9b)**



Compound **8b** (1,461 g, 80%$_m$ **8b**, 2,675 mmol) was prepared in a 50 mL round-bottomed flask and dissolved in dry THF (18 mL). The solution was degassed by flushing with argon under stirring and it was cooled to 0 °C. Thereafter, TBAF solution (1 M in THF, 0.820 mL, 0.820 mmol) was added dropwise at 0 °C. The mixture turning dark brown and was stirred for 1 h before it was allowed to warm up to room temperature. The solution was filtered through a layer of silica gel and the solvent was removed on a rotary evaporator. The residue was then purified on a reversed phase column on the IntelliFlash system in two runs. The product was obtained as a yellow oil. 0.886 g (91%).

molecular weight: 364.50 g/mol
chemical formula: $C_{23}H_{24}O_2S$
exact mass 364.15, ESI-MS positive (m/z): 365.1552 (M+H, calc. 365.1570)
387.1380 (M+Na, calc. 387.1389)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.98-7.95 (m, 2H, H15), 7.58-7.55 (m, 2H, H14), 7.46 (s, 1H, H3), 3.19 (s, 1H, H12), 2.82-2.76 (m, 2H, H7/H9), 2.72-2.66 (m, 2H, H7/H9), 2.50 (s, 3H, H5), 2.02 (qi, 2H, H8, J=7.5 Hz), 1.61 (s, 9H, H19).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 165.6 (C17), 145.7 (C6), 138.5 (C4), 138.3 (C13), 137.7 (C1), 135.4 (C2), 130.4 (C16), 130.2 (C15), 125.3 (C3), 125.0 (C14), 120.0 (C10), 82.4 (C12), 81.8 (C11), 81.0 (C18), 37.8 (C7,C9), 28.4 (C19), 23.2 (C8), 15.7 (C5).

2.6.4. Azides

2.6.4.1. Alkyl azides

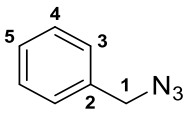
Except for azidoethane (**10i**), all alkyl and benzyl azides were prepared using a general procedure as described by Q. Zhang et al. [9] [138]. Since most of the small alkyl azides were not or only very poorly detected in the ESI, the syntheses of the compounds known without exception from the literature were validated by the ^{1}H-NMR spectra and their comparison with those of the respective reactants (corresponding bromo compound).

General approach for the synthesis of alkyl azides:

The respective alkyl bromide (1 eq.) was prepared in a 100 mL round bottomed flask and dissolved in DMSO. Sodium azide (1-2 eq) was added and the mixture was stirred overnight under light exclusion.

The mixture was diluted with water (20 ml / 5.85 mol) and extracted three times with Diethyl ether before the combined organic phases were washed with water (4x) and dried via $MgSO_4$. Thereafter the solvent was eliminated by rotary evaporator whereby the temperature was kept below 40 °C. The product was obtained in high purity without further purification.

(Azidomethyl)benzene **(10a)**



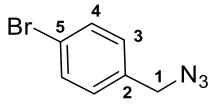
From α-Bromotoluene (1.00 g, 5.85 mmol) and sodium azide (0.65 g, 10 mmol) in DMSO (20 mL) the product was obtained as a colorless oil. 0.73 g (94 %).

molecular weight: 133.15 g/mol
chemical formula: $C_7H_7N_3$
exact mass 133.06, ESI-MS positive (m/z): 423.2 (3M+H, calc. **423.19**)

^{1}H-NMR (300MHz, $CDCl_3$):

δ (ppm) = 7.49-7.35 (m, 5H, H3,H4,H5), 4.36 (s, 2H, H1).

1-(Azidomethyl)-4-bromobenzene **(10b)**

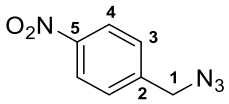


A mixture of α,4-Dibromotoluene (1.00 g, 4.00 mmol) and sodium azide (0.40 g, 6.2 mmol) in DMSO (20 mL) was used. The combined organic phases were washed additional to the general approach with sat. NaCl-solution. The product was obtained as a colorless oil. 0.69 g (82 %).

molecular weight: 212.05 g/mol
chemical formula: $C_7H_6BrN_3$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.55-7.48 (m, 2H, H4), 7.22-7.16 (m, 2H, H3), 4.31 (s, 2H, H1).

1-(Azidomethyl)-4-nitrobenzene **(10c)**

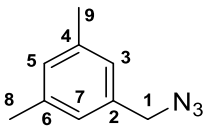


From α-Bromo-4-nitrotoluene (1.00 g, 4.63 mmol) and sodium azide (0.40 g, 6.2 mmol) in DMSO (20 mL) the product was obtained as a yellow-orange oil. 780 mg (95 %).

molecular weight: 178.15 g/mol
chemical formula: $C_7H_6N_4O_2$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 8.27-8.21 (m, 2H, H4), 7.53-7.47 (m, 2H, H3), 4.50 (s, 2H, H1).

1-(Azidomethyl)-3,5-dimethylbenzene **(10d)**

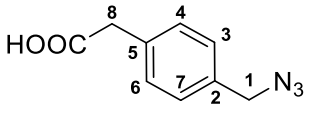


From 1-(Bromomethyl)-3,5-dimethylbenzol (1.00 g, 5.02 mmol) and sodium azide (0.327 g, 5.02 mmol) in DMSO (20 mL) the product was obtained as a colorless oil. 693 mg (86 %).

molecular weight: 161.21 g/mol
chemical formula: $C_9H_{11}N_3$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 6.98 (m, 1H, H5), 6.93 (m, 2H, H3,H7), 4.26 (s, 2H, H1), 2.33 (s, 6H, H8,H9).

2-(4-(Azidomethyl)phenyl)acetic acid **(10e)**

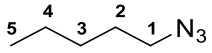


From (4-(bromomethyl)phenyl)acetic acid (1.50 g, 6.55 mmol) and sodium azide (0.740 g, 11.0 mmol) in DMSO (20 mL) the product was obtained as a colorless oil. 0.76 g (61 %).

molecular weight: 191.19 g/mol
chemical formula: $C_9H_9N_3O_2$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.34.7.26 (m, 4H, H3,H4), 4.33 (s, 2H, H1), 3.67 (s, 2H, H8).

1-Azidopentane **(10f)**



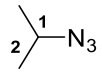
A mixture of 1-Bromopentane (0.84 mL, 1.0 g, 6.8 mmol) and sodium azide (0.650 g, 10.0 mmol) in DMSO (20 mL) was used. After extraction in diethyl ether/water the combined organic phases were washed with water and sat. NaCl-solution. It was dried via $MgSO_4$ and the clear colorless solution was concentrated slowly and carefully by rotary evaporator to a volume of 0.1 - 0.2 mL. The product was obtained as a slightly yellowish oil that still contained small amounts of diethyl ether. 0.1 - 0.2 mL. 56.18 $\%_{mol}$ product in diethyl ether.

Note: Further evaporation of the ether resulted in the loss of significant amounts of the volatile product. Furthermore, the remaining amounts of diethyl ether did not cause any problems in the next stage of the synthesis (batch was made in THF). Therefore, the solvent was not further removed.

molecular weight: 113.16 g/mol
chemical formula: $C_5H_{11}N_3$

^{1}H-NMR (300 MHz, CDCl3):
δ (ppm) = 3.30-3.21 (m, 2H, H1), 1.65-1.55 (m, 3H, H5), 1.38-1.30 (m, 4H, H3,H4), 0.95-0.87 (m, 2H, H2).

2-Azidopropane **(10g)**



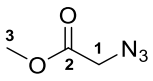
A mixture of 2-Bromopropane (0.77 mL, 0.67 g, 7.8 mmol) and sodium azide (0.801 g, 12.3 mmol) in DMSO (20 mL) was used. After extraction in diethyl ether/water the combined organic phases were washed with water and sat. NaCl-solution. It was dried via $MgSO_4$ and the clear colorless solution was concentrated slowly and carefully by rotary evaporator to a volume of 0.1 mL. The product was obtained as a slightly yellowish oil that still contained high amounts of diethyl ether. Further concentration to 0.1 - 0.2 mL led to just small amounts of diethyl ether. 0.1 - 0.2 mL, 24.22 $\%_{mol}$ product in diethyl ether.

Note: Further evaporation of the ether resulted in the loss of significant amounts of the volatile product. Furthermore, the remaining amounts of diethyl ether did not cause any problems in the next stage of the synthesis (batch was made in THF). Therefore, the solvent was not further removed.

molecular weight: 85.11 g/mol
chemical formula: $C_3H_7N_3$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 3.61 (sp, 1H, H1, $^3J_{(H,H)}$=6.5 Hz), 1.23 (d, 6H, H2, $^3J_{(H,H)}$=6.5 Hz).

Methyl-2-azidoacetate **(10h)**



Methyl bromoacetate (1.50 g, 9.81) was dissolved in DMSO (25 mL) in a 100 mL round bottom flask. Sodium azide (1.29 g, 19.8 mmol) was added and the mixture was stirred for 4 days at room temperature with the exclusion of light.
The solution was extracted with diethyl ether (3 x 150 ml) and water, the combined organic phases were washed three times with water and then dried over MgSO4. The solvent was removed on a rotary evaporator, avoiding temperatures above 40 ° C. The product was obtained as a colorless liquid. 0.99 g (100%).

molecular weight: 115.09 g/mol
chemical formula: $C_3H_5N_3O_2$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 3.89 (s, 2H, H1), 3.81 (s, 3H, H3).

Azidoethane in THF **(10i)**

Azidoethane was used in a slightly modified procedure as described by Swetha *et al.*[10]

Sodium azide (14.3 g, 220 mmol) in water (28 mL) was prepared in a 100 mL round-bottom flask. Ethyl bromide (11.20 mL, 16.35 g, 150.0 mmol) was dissolved in THF (58 mL) and the solution was added to the sodium azide solution under stirring. The mixture was then refluxed under vigorous stirring overnight.
After cooling to room temperature, the mixture was transferred to a separatory funnel and the aqueous phase was separated off. The organic phase was washed once with water and then dried via $MgSO_4$. The filtrate was not further concentrated, but freshly prepared and used as a solution in the next synthesis step. The product concentration was estimated by ^{1}H-NMR spectroscopy (ethylazide: THF in $CDCl_3$). A colorless solution with an ethylazide concentration of 2.38 mol / L was obtained. 56.1 ml (85%).

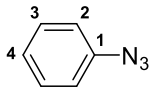
molecular weight: 71.08 g/mol
chemical formula: $C_2H_5N_3$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 3.20 (q, 2H, H1, $^3J_{H,H}$ = 7.2 Hz), 1.16 (t, 3H, H2, $^3J_{H,H}$ = 7.2 Hz).

^{13}C-NMR (75 MHz, $CDCl_3$):
δ (ppm) = 45.7 (C1), 13.2 (C2).

2.6.4.2. Phenyl azides

Azidobenzene **(10j)**



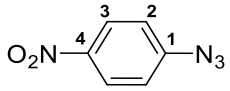
Synthesized in a general approach described by Zhang *et al.* [9]. Aniline (0.98 mL, 1.00 g, 10.7 mmol) was mixed with water (50 mL) in a 100 mL round bottom flask. The solution was stirred at room temperature while HCl (37%, 11.2 mL, 135 mmol) was added dropwise. The finally clear solution was cooled to 0 °C and then $NaNO_2$ (0.740 g in 10 mL water, 10.7 mmol) was added slowly and in portions, while the temperature in the reaction mixture was kept below 3 °C.

It was stirred for 10 min before sodium azide (0.838 g, 12.9 mmol) was added slowly and in small portions. The mixture was stirred for 2 h before the ice bath was removed. Thereafter, stirring was continued for a further hour at room temperature.
The slightly yellowish solution was extracted with diethyl ether (1 x 50, 2 x 25 mL) and the combined organic phases were washed with water (2 x 50 mL) and then dried via Na_2SO_4. The solvent was removed on a rotary evaporator to give the product as a yellow oil. 0.99 g (78%).

molecular weight: 119.13 g/mol
chemical formula: $C_6H_5N_3$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.40-7.33 (m, 2H, H3), 7.18-7.11 (m, 1H, H4), 7.06-7.01 (m, 2H, H2).

1-Azido-4-nitrobenzene **(10k)**



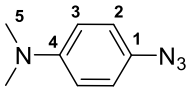
Synthesized in a general approach described by Zhang *et al* [9]. 4-Nitroaniline (1.50 g, 10.9 mmol) was placed in a 100 mL round-bottom flask and then mixed with conc. HCl (1.70 mL, 20.0 mmol). Under ice cooling, a solution of $NaNO_2$ (690 mg, 10.0 mmol) in water (4 mL) was slowly and dropwise added to keep the temperature below 5 °C. The reaction mixture was stirred at 0 °C for 10 min and then a solution of sodium azide (650 mg, 10.0 mmol) in water (5 ml) was added dropwise. The temperature was controlled by the addition rate and kept below 5 °C. A slight gas formation and the precipitation of a yellow solid were observed during the addition. The suspension was finally stirred at 0 °C for 20 min and then at room temperature for 3 h.

The mixture was extracted with ethyl acetate (3 x 75 mL) and the combined organic phases were dried via Na_2SO_4. The solvent was removed on a rotary evaporator and the crude product was purified by column chromatography (silica gel, DCM / cyclohexane 1:1). The product was obtained as a yellow solid. 1.28 g (72%).

molecular weight: 164.12 g/mol
chemical formula: $C_6H_4N_4O_2$

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 8.11-8.03 (m, 2H, H3), 6.66-6.59 (m, 2H, H2).

4-Azido-N,N-dimethylaniline **(10l)**[11,12]



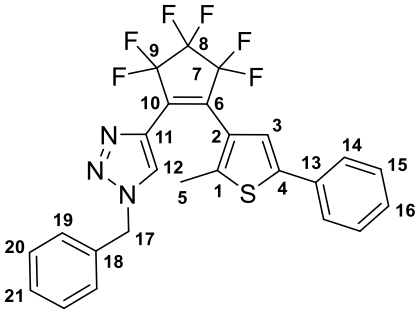
In a 50 mL Schlenk flask 4-bromo-N, N-dimethylaniline (1.50 g, 7.50 mmol), sodium azide (980 mg, 15.1 mmol), sodium ascorbate (74 mg, 0.37 mol) and copper(I)iodide (140 mg, 0.735 mmol) were prepared and then dissolved in an ethanol-water mixture (7:3, 15 mL). N,N-Dimethyl ethylenediamine (120 µL, 98.3 mg, 1.12 mmol) was added and the greenish mixture was degassed by flushing with argon while stirring. The mixture was then refluxed at 85 °C for 45 min.
After cooling to room temperature, water (10 ml) was added. The mixture was stirred before the phases were separated. The aqueous phase was extracted with ethyl acetate (5 x 80 mL). The combined organic phases were washed with water (3 x 150 mL) and then dried via $MgSO_4$. The solvent was removed on a rotary evaporator and the crude product was purified by column chromatography (silica gel, cyclohexane / ethyl acetate 9:1). The product was obtained as a yellow solid. 1.10 g (91%).

molecular weight: 162.20 g/mol
chemical formula: $C_8H_{10}N_4$
exact mass 162.09, ESI-MS positive (m/z): 163.1 (M+H, calc. 163.1)

^{1}H-NMR (300 MHz, $CDCl_3$):
δ (ppm) = 7.78-7.74 (m, 2H, H2), 7.71-7.65 (m, 2H, H3), 1.58 (s, 6H, H5).

2.6.5. Triazole photoswitches

1-Benzyl-4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1H-1,2,3-triazole **(pF_{PS} 1)**



A microwave vial was heated in argon flow before dry THF (2.3 mL) was added. The solvent was degassed by flushing with argon under stirring. Compound **6a** (200 mg, 0.537 mmol), (azidomethyl)benzene **10a** (72 mg, 0.54 mmol) and copper(I)iodide (50 mg, 0.26 mmol) were added in argon counterflow. The mixture was stirred for 5 min and then the catalyst phen$(PPh_3)_2Cu(I)NO_2$·DCM (12.6 mg, 14.4 µmol) was added. The vessel was closed and the mixture was stirred at room temperature overnight under light exclusion.
The mixture was transferred to a round bottom flask with silica gel and the solvents were removed on a rotary evaporator. It was then purified by column chromatography (silica gel, gradient: cyclohexane, cyclohexane / ethyl acetate 20:1) and the product was isolated as a brownish oil, which crystallized very slowly. 266 mg (98%).

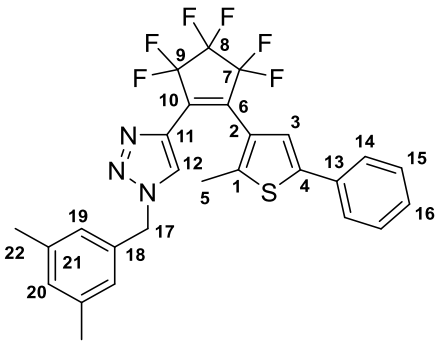
molecular weight: 505.48 g/mol
chemical formula: $C_{25}H_{17}F_6N_3S$
exact mass 505.10, ESI-MS positive (m/z): 528.0932 (M+Na, calc. 528.0940)
1033.1965 (2xM+Na, calc. 1033.1987)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.54-7.51 (m, 2H, H14), 7.40-7.36 (m, 2H, H15), 7.35-7.28 (m, 5H, H12, H16, H20, H21), 7.22-7.19 (m, 2H, H19), 7.10 (s, 1H, H3), 5.50 (s, 2H, H17), 2.13 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 142.81 (C4), 140.40 (C1), 136.60 (C11), 134.43 (CF2/C6/10), 133.77 (C18), 133.54 (C13), 132.02 (CF2/C6/10), 129.42 (C20), 129.29 (C21), 129.10 (C15), 128.27 (C19), 128.00 (C16), 125.73 (C14), 125.24 (C2), 124.76 (C12), 122.50 (C3), 116.14 (CF2/C6/10), 114.10 (CF2/C6/10), 113.27 (CF2/C6/10), 111.10 (CF2/C6/10), 54.55 (C17), 14.33 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.4 - -110.5 (m, 2F, F7/F9), -110.8 - -110.9 (m, 2F, F7/F9), -131.3 (m, 2F, F8).

1-(3,5-Dimethylbenzyl)-4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1H-1,2,3-triazole **(pF_{PS} 2)**



1-(Azidomethyl)-3,5-dimethylbenzene **10d** (78.1 mg, 0.393 mmol) was placed in a lockable microwave vial and dissolved in dry THF (0.2 mL). A solution of compound **6a** (135.5 mg, 0.364 mmol) in dry THF (1.2 mL) was added and the mixture was degassed by flushing with argon under stirring. Copper(I)iodide (9.6 mg, 50 µmol) and the catalyst phen(PPh_3)$_2$Cu(I)NO_2·DCM (8.3 mg, 9.5 µmol) were added in argon counterflow and then the vessel was closed. The mixture was stirred at room temperature overnight under light exclusion.
The mixture was transferred to a round bottom flask with silica gel and the solvents were removed on a rotary evaporator. After purification by column chromatography (silica gel, gradient: cyclohexane cyclohexane / ethyl acetate 20:1-20:5), the product was obtained as a brown solid. 94.8 mg (49%).

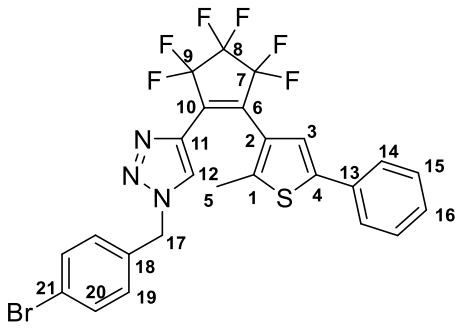
molecular weight: 533.54 g/mol
chemical formula: $C_{27}H_{21}F_6N_3S$
exact mass 533.14, ESI-MS positive (m/z): 556.1256 (M+Na, calc. 556.1253)
1089.2608 (2M+Na, calc.1089.2800)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.54-7.50 (m, 2H, H14), 7.40-7.36 (m, 2H, H15), 7.32-7.28 (m und s, 2H, H16, H12), 7.10 (s, 1H, H3), 6.94 (s, 1H, H20), 6.81 (s, 2H, H19), 5.40 (s, 2H, H17), 2.25 (s, 6H, H22), 2.12 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 142.81 (C4), 140.24 (C1), 139.18 (C21), 136.54 (C11), 133.56 (C18), 133.53 (C13), 130.89 (C20), 129.10 (C15), 128.00 (C16), 126.12 (C19), 125.69 (C14), 125.29 (C2), 124.77 (C12), 122.49 (C3), 54.56 (C17), 21.29 (C22), 14.27 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.4 - -110.5 (m, 2F, F7/F9), -110.8 – 110.9 (m, 2F, F7/F9), -131.2 - -131.3 (m, 2F, F8).

1-(4-Bromobenzyl)-4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1H-1,2,3-triazole **(pF_{PS} 3)**



1-(Azidomethyl)-4-bromobenzene **10b** (83.3 mg, 0.393 mmol) was placed in a lockable microwave vial and dissolved in dry THF (0.2 mL). A solution of compound **6a** (135.5 mg, 0.364 mmol) in dry THF (1.2 L) was added and the mixture was then degassed by flushing with argon under stirring. Copper(I)iodide (11.5 mg, 60.4 µmol) was added in argon counterflow, and the catalyst phen$(PPh_3)_2Cu(I)NO_2$·DCM (11.0 mg, 12.6 µmol) was added. The reaction vessel was closed and stirred overnight at room temperature under light exclusion.
The mixture was then transferred to a round bottom flask and after the addition of silica gel the solvents were removed on a rotary evaporator. Purification by column chromatography (silica gel, gradient: cyclohexane - cyclohexane / ethyl acetate 20:1-20:8) gave the product as a brown solid. 163 mg (76%).

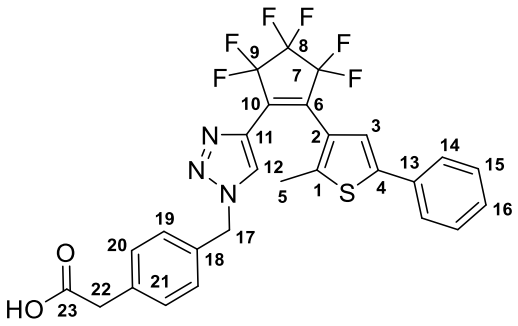
molecular weight: 584.38 g/mol
chemical formula: $C_{25}H_{16}BrF_6N_3S$
exact mass 583.02, ESI-MS positive (m/z): 606.0012 (M+Na, calc. 606.0045)
1189.0132 (2M+Na, calc. 1189.020)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.55-7.51 (m, 2H, H14), 7.47-7.44 (d, 2H, H20), 7.41-7.37 (m, 2H, H15), 7.34 (s, 1H, H12), 7.33-7.29 (mt, 1H, H16), 7.11-7.07 (s und m, 3H, H3, H19), 5.45 (s, 2H, H17), 2.15 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 124.90 (C4), 140.40 (C1), 136.76 (C11), 133.47 (C13), 132.75 (C18), 132.64 (C20), 129.87 (C19), 129.16 (C15), 128.07 (C16), 125.71 (C14), 125.22 (C2), 124.66 (C12), 123.58 (C21), 122.48 (C3), 53.83 (C17), 14.37 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.4 - -110.5 (m, 2F, F7/F9), -110.8 - -110.9 (m, 2F, F7/F9), -131.3 (m, 2F, F8).

2-(4-((4-(3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1H-1,2,3-triazole-1-yl)methyl)phenyl)acetic acid **(pF_{PS} 4)**



A microwave vial was heated under argon. Compound **6a** (120 mg, 0.322 mmol) was added and dissolved in dry THF (1.55 mL). 2-(4-(Azidomethyl)phenyl)ethanoic acid **10e** (67.49 mg, 0.3530 mmol) was added and the solution was then degassed by flushing with argon under stirring. Copper(I)iodide (10.92 mg, 57.34 µmol) was added in argon counterflow, the mixture was stirred for 10 min and then the catalyst phen$(PPh_3)_2Cu(I)NO_2$·DCM (7.75 mg, 8.88 µmol) was added.
The vessel was closed and the mixture was then stirred for two days at room temperature under light exclusion.
The solvent was then removed in a rotary evaporator and the residue was purified by column chromatography (silica gel, gradient: cyclohexane / ethyl acetate 9:1 – ethyl acetate – ethyl acetate / methanol 5:1). The product was obtained as a brown oil. 140 mg (77%).

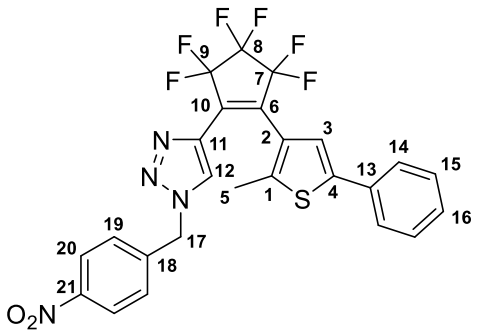
molecular weight: 563.52 g/mol
chemical formula: $C_{27}H_{19}F_6N_3O_2S$
exact mass 563.11, ESI-MS positive (m/z): 586.0981 (M+Na, calc. 586.0994)
1149.2068 (2xM+Na, calc.1149.2097)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.55-7.51 (m, 2H, H14), 7.40-7.35 (m, 2H, H15), 7.34 (s, 1H, H12), 7.32-7.27 (m, 2H, H16,H23), 7.24 (d, 2H, H20), 7.14 (d, 2H, H19), 7.10 (s, 1H, H3), 5.47 (s, 2H, H17), 3.60 (s, 2H, H22), 2.12 (s. 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 175.8 (C23), 142.8 (C4), 140.5 (C1), 136.8 (C11), 134.5 (C21), 133.5 (C13), 133.0 (C18), 130.5 (C20), 129.1 (C15), 128.6 (C19), 128.0 (C16), 125.7 (C14), 125.2 (C2), 124.8 (C12), 122.5 (C3), 54.2 (C17), 40.4 (C22), 14.3 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.4 - -110.5 (m, 2F, F7/F9), -110.8 - -110.9 (m, 2F, F7/F9), -131.3 (m, 2F, F8).

4-(3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1-(4-nitrobenzyl)-1H-1,2,3-triazole **(pF_{PS} 5)**



1-(Azidomethyl)-4-nitrobenzene **10c** (69.9 mg, 0.392 mmol) was placed in a microwave vial and dissolved in dry THF (0.2 mL). A solution of compound **6a** (136 mg, 0.364 mmol) in dry THF (1.3 mL) was added and the mixture was then degassed by flushing with argon under stirring. Copper(I)iodide (11 mg, 58 µmol) was added under argon counterflow and the catalyst phen$(PPh_3)_2$Cu(I)NO_2·DCM (9.0 mg, 10 µmol) was added. The vessel was then sealed and stirred for 63 h at room temperature under light exclusion.
The mixture was transferred with diethyl ether into a round bottom flask with silica gel and the solvents were removed on a rotary evaporator. Purification by column chromatography (silica gel, gradient: cyclohexane cyclohexane / ethylacetate 20:1 – 5:1) gave the product as a yellow solid. 165 mg (83%).

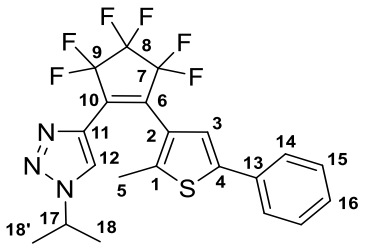
molecular weight: 550.48 g/mol
chemical formula: $C_{25}H_{16}F_6N_4O_2S$
exact mass 550.09, ESI-MS positive (m/z): 573.0796 (M+Na, calc. 573.0790)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 8.20-8.15 (m, 2H, H20), 7.54-7.49 (m, 2H, H14), 7.44 (s, 1H, H12), 7.40-7.34 (m, 4H, H15,H19), 7.33-7.28 (m, 1H, H16), 7.10 (s, 1H, H3), 5.62 (s, 2H, H17), 2.19 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 148.4 (C21), 143.0 (C4), 140.6 (C18), 140.4 (C1), 137.0 (C11), 133.3 (C13), 129.2 (C15), 128.9 (C19), 128.2 (C16), 125.6 (C14), 125.2 (C2), 124.9 (C12), 124.6 (C20), 122.4 (C3), 53.4 (C17), 14.4 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.5 - -110.6 (m, 2F, F7/F9), -110.8 - -110.9 (m, 2F, F7/F9), -131.3 (m, 2F, F8).

4-(3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1-isopropyl-1H-1,2,3-triazole **(pF_{PS} 6)**



A microwave vial was heated under argon flow and compound **6a** (100 mg, 0.269 mmol) was placed in it. Copper(I)iodide (0.9 mg, 4.7 µmol) and the catalyst phen$(PPh_3)_2Cu(I)NO_2$·DCM (6.8 mg, 7.8 µmol) was added and the vessel was then sealed, the solids were dissolved in dry THF (1.5 mL) and the solution was then degassed by flushing with argon under stirring while 2-azidopropane **10g** (25.2 mg, 0.296 mmol) was added and the mixture was then stirred at room temperature overnight under light exclusion.
The mixture was transferred into a round-bottomed flask with diethyl ether and, after the addition of silica gel, the solvents were removed on a rotary evaporator. The mixture was then purified by column chromatography (silica gel, gradient: cyclohexane cyclohexane / ethylacetate 20:1 20:6). The product was isolated as a brown, highly viscous oil, which slowly crystallized when stored at -20 °C. 94.8 mg (77%).

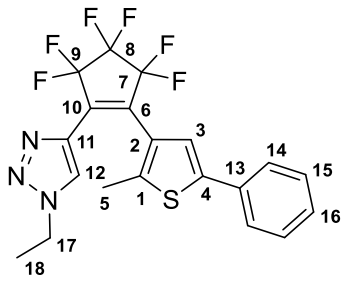
molecular weight: 457.44 g/mol
chemical formula: $C_{21}H_{17}F_6N_3S$
exact mass 457.10, ESI-MS positive (m/z): 480.0916 (M+Na, calc. 480.0940)
937.1959 (2M+Na, calc. 937.2000)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.58-7.55 (m, 2H, H14), 7.53 (s, 1H, H12), 7.40-7.36 (m, 2H, H15), 7.31-7.27 (m, 1H, H16), 7.17 (s, 1H, H3), 4.80 (sp, 1H, H17, $^3J_{(H,H)}$ = 6.7 Hz), 2.21 (s, 3H, H5), 1.56 (d, 6H, H18, $^3J_{(H,H)}$ = 6.7 Hz).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 142.59 (C4), 140.63 (C1), 135.93 (C11), 133.67 (C13), 129.11 (C15), 127.94 (C16), 125.75 (C14), 125.39 (C2), 122.70 (C3), 122.47 (C12), 116.19 (C6/C10), 111.11 (C6/C10), 53.72 (C17), 23.04 (C18), 14.49 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.3 - -110.4 (m, 2F, F7/F9), -110.8 - -110.9 (m, 2F, F7/F9), -131.3 - -131.4 (m, 2F, F8).

1-Ethyl-4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1H-1,2,3-triazole **(pF_{PS} 7)**



A microwave vial was heated under argon flow and compound **6a** (79 mg, 0.21 mmol) was dissolved in dry THF (0.89 mL). The light brown solution was degassed by flushing with argon under stirring before a solution of azidoethane in THF **10j** (2.38 M in THF, 0.15 mL, 0.357 mmol) was added. The mixture was stirred for 10 min before copper(I)iodide (17 mg, 89 µmol) was added and after stirring for further 10 min the catalyst phen$(PPh_3)_2Cu(I)NO_2$·DCM (4.5 mg, 5.2 µmol) was added. The vessel was closed and stirred overnight at room temperature under light exclusion. After 20 minutes the mixture turned to a deep red color.
Water was added, the phases separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried via $MgSO_4$ and the solvents were removed on a rotary evaporator. The brown oil obtained was purified by column chromatography (silica gel, gradient: cyclohexane, cyclohexane / ethyl acetate 5:1) to obtain the product as a brown solid. 77.1 mg (49%).

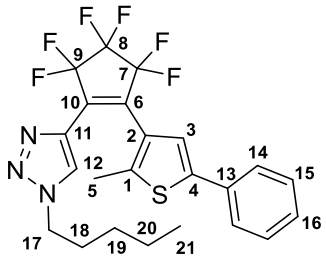
molecular weight: 443.41 g/mol
chemical formula: $C_{20}H_{15}F_6N_3S$
exact mass 443.09, ESI-MS positive (m/z): 466.0795 (M+Na, calc. 466.0783)
909.1671 (2M+Na, calc. 909.1674)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.59-7.55 (m, 2H, H14), 7.52 (s, 1H, H12), 7.40-7.36 (m, 2H, H15), 7.32-7.27 (m, 1H, H16), 7.17 (s, 1H, H3), 4.41 (q, 2H, H17, $^3J_{(H,H)}$ = 7.2 Hz), 2.22 (s, 3H, H5), 1.53 (t, 3H, H18, $^3J_{(H,H)}$ =7.2 Hz).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 142.69 (C4), 140.54 (C1/C2), 136.25 (C11), 133.61 (C13), 129.12 (C15), 127.98 (C16), 125.74 (C14), 125.36 (C1/C2), 124.15 (C12), 122.64 (C3), 45.80 (C17), 15.54 (C18), 14.45 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.4 - -110.5 (m, 2F, F7/F9), -110.8 - -110.9 (m, 2F, F7/F9), -131.3 - -131.4 (m, 2F, F8).

4-(3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1-pentyl-1H-1,2,3-triazole **(pF_{PS} 8)**



A microwave vial was heated under argon flow and compound **6a** (100 mg, 0.269 mmol) copper(I)iodide (0.9 mg, 4.73 µmol) and the catalyst phen(PPh_3)$_2$Cu(I)NO_2·DCM (6.8 mg, 7.8 µmol) submitted. The vessel was closed, the solids were then dissolved in dry THF (1.5 mL) and the solution was degassed by flushing with argon under stirring. 1-Azidopentane **10f** (33.4 mg, 0.295 mmol) was added and the mixture was stirred overnight at room temperature under light exclusion.
The mixture was transferred into a round-bottomed flask with diethyl ether and, after the addition of silica gel, the solvents were removed on a rotary evaporator. After column chromatography (silica gel, gradient: cyclohexane / ethyl acetate 20:1 20:6), the product was isolated as a brown solid. 132 mg (quant%).

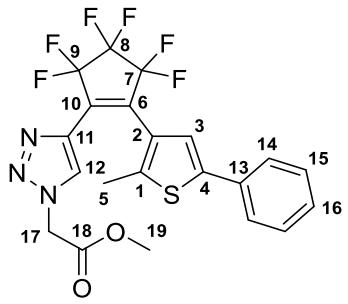
molecular weight: 485.49 g/mol
chemical formula: $C_{23}H_{21}F_6N_3S$
exact mass 485.14, ESI-MS positive (m/z): 508.1235 (M+Na, calc. 508.1253)
993.2587 (2M+Na, calc. 993.2800)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.58-7.55 (m, 2H, H14), 7.47 (s, 1H, H12), 7.40-7.36 (m, 2H, H15), 7.31-7.28 (m, 1H, H16), 7.17 (s, 1H, H3), 4.33 (t, 2H, H17, $^3J_{(H,H)}$ = 7.2 Hz) 2.21 (s, 3H, H5), 1.87 (tvt, 2H, H18, $^3J_{(H,H)}$ = 7.40 Hz) 1.35-1.21 (m, 4H, H20, H19), 0.87 (t, 3H, H21, $^3J_{(H,H)}$ = 7.3 Hz).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 142.75 (C4), 140.45 (C1), 136.16 (C11), 133.60 (C13), 129.13 (C15), 128.00 (C16), 125.75 (C14), 125.39 (C2), 124.64 (C12), 122.63 (C3), 50.75 (C17), 29.95 (C18), 28.58 (C19), 22.13 (C20), 14.42 (C5), 13.92 (C21).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.4 (m, 2F, F7/F9), -110.8 - -110.9 (m, 2F, F7/F9), -131.3 (m, 2F, F8).

Methyl-2-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1H-1,2,3-triazole-1-yl)acetate **(pF_{PS} 9)**



A microwave vial was heated under argon flow and compound **6a** (120 mg, 0.322 mmol) was dissolved in dry THF (1.55 mL). Methyl 2-azidoacetate **10h** (41.0 mg, 0.356 mmol) was added and then the solution was degassed by flushing with argon under stirring. Copper(I)iodide (10.92 mg, 57.34 µmol) was added in a protective gas countercurrent, the mixture was stirred for 10 min and then the catalyst phen(PPh_3)$_2$Cu(I)NO_2·DCM (7.75 mg, 8.88 µmol) was added. The vessel was then closed and the mixture was stirred at room temperature for two days under light exclusion.
The solvent was removed on a rotary evaporator and the residue was purified by column chromatography (silica gel, gradient: cyclohexane / ethyl acetate 9:1 - 5:1). The product was obtained as a beige solid. 150 mg (96%).

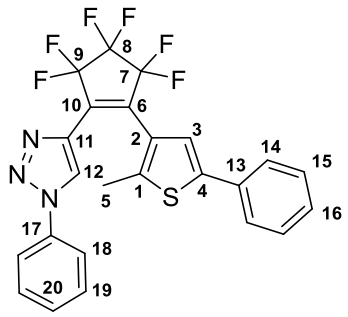
molecular weight: 487.02 g/mol
chemical formula: $C_{21}H_{15}F_6N_3O_2S$
exact mass 487.08, ESI-MS positive (m/z): 488.0853 (M+H, calc. 488.0862)
510.0681 (M+Na, calc. 510.0681)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.65 (s, 1H, H12), 7.59-7.55 (m, 2H, H14), 7.41-7.36 (m, 2H, H15) 7.32-7.28 (m, 1H, H16), 7.19 (s, 1H, H3), 5.17 (s, 2H, H17), 3.80 (s, 3H, H19), 2.21 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 166.15 (C18), 142.87 (C4), 140.73 (C1), 136.55 (C11), 133.54 (C13), 129.13 (C15), 128.03 (C16), 126.32 (C12), 125.75 (C14), 125.16 (C2), 122.52 (C3), 53.40 (C19), 50.87 (C17), 14.39 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.5 - -110.6 (m, 2F, F7/F9), -110.7 - -110.8 (m, 2F, F7/F9), -131.3 (m, 2F, F8).

4-(3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1-phenyl-1H-1,2,3-triazole **(pF_{PS} 10)**



A sealable microwave vial was heated under argon flow and dry THF (1.7 mL) was added. The solvent was degassed by flushing with argon under stirring and in argon counterflow azidobenzene **10k** (110 mg, 0.923 mmol), compound **6a** (150 mg, 0.403 mmol) and copper(I)iodide (16.37 mg, 85.95 µmol) were added. The mixture was stirred for 5 min and then the catalyst phen$(PPh_3)_2Cu(I)NO_2$·DCM (12.6 mg, 14.4 µmol) was added. The initially yellowish solution turned dark within 10 min after the catalyst had been added. The vessel was closed and the mixture was stirred at room temperature overnight under light exclusion.
The solution was filtered through a thin layer of silica gel and the solvent was removed on a rotary evaporator. The residue was then purified by column chromatography (silica gel, gradient: cyclohexane, cyclohexane / ethyl acetate 10:1). The product was obtained as a yellow-brown solid. 163 mg (82%).

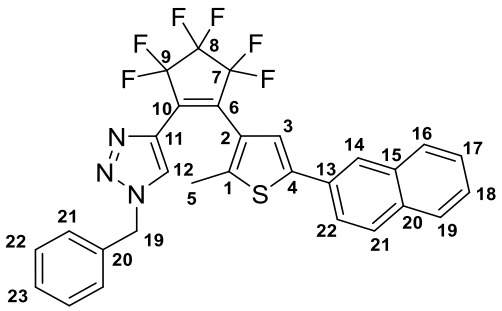
molecular weight: 491.46 g/mol
chemical formula: $C_{24}H_{15}F_6N_3S$
exact mass 491.09, ESI-MS positive (m/z): 514.0784 (M+Na, calc. 514.0783)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.99 (s, 1H, H12), 7.69-7.65 (m, 2H, H18), 7.60-7.56 (m, 2H, H14), 7.55-7.51 (m, 2H, H19), 7.49-7.46 (m, 1H, H20), 7.40-7.36 (m, 2H, H15), 7.32-7.28 (m, 1H, H16), 7.22 (s, 1H, H3), 2.27 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 143.60 (C6), 142.79 (C4), 140.81 (C1/2), 136.98 (C11), 136.32 (C17), 133.61 (C13), 130.13 (C19), 129.69 (C20), 129.12 (C15), 128.00 (C16), 125.79 (C14), 125.25 (C1/C2), 122.61 (C3 und C12), 120.82 (C18), 14.59 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.4 - -110.5 (m, 2F, F7/F9), -110.7 - -110.8 (m, 2F, F7/F9), -131.2 - -131.3 (m, 2F, F8).

1-Benzyl-4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-(naphthalene-2-yl)thiophene-3-yl)cyclopent-1-ene-1-yl)-1H-1,2,3-triazole **(pF_{PS} 11)**



A microwave vial was heated under argon flow and the (azidomethyl)benzene **10a** (48.2 mg, 0.3619977 mmol)) was dissolved in THF (1.6 mL). The solution was degassed by flushing with argon under stirring and then Compound **6c** (150 mg, 0.355 mmol) was added. Copper(I)iodide (11.4 mg, 59.9 µmol) was added in argon counterflow, the mixture was stirred and then the catalyst phen$(PPh_3)_2Cu(I)NO_2$·DCM (8.10 mg, 9.28 µmol) was added. The vessel was then sealed and the mixture was stirred overnight at room temperature under light exclusion.
The mixture was transferred into a round-bottomed flask with diethyl ether and, after the addition of silica gel, the solvents were removed on a rotary evaporator. After purification by column chromatography (silica gel, gradient: cyclohexane-cyclohexane / ethyl acetate 10:1), the product was obtained as a brownish oil which crystallized after storage at -20 ° C. 194 mg (98%).

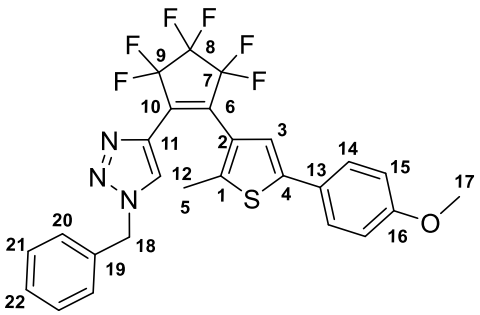
molecular weight: 555.54 g/mol
chemical formula: $C_{29}H_{19}F_6N_3S$
exact mass 555.12, ESI-MS positive (m/z): 578.1108 (M+Na, calc. 578.1096)
1133.2291 (2M+Na, calc. 1133.2300)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.96 (b, 1H, H14), 7.87-7.82 (m, 3H, H16,H19,H21), 7.67-7.63 (m, 1H, H22), 7.53-7.46 (m, 2H, H17, H18), 7.36 (s, 1H, H12), 7.33-7.27 (m, 3H, H26, H27), 7.25-7.18 (s und m, 3H, H3, H25), 5.50 (s, 2H, H23), 2.17 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 142.9 (C4), 140.7 (C1), 136.4 (C11), 133.8 (C24), 133.7 (C15), 133.0 (C20), 130.9 (C13), 129.4 (C26), 129.3 (C27), 128.8 (C21), 128.3 (C25), 128.2 (C16), 127.9 (C19), 126.9 (C17/C18), 126.4 (C17/C18), 125.4 (C2), 124.8 (C12), 124.2 (C14), 124.0 (C22), 122.9 (C3), 54.6 (C23), 14.4 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.3 - -110.4 (m, 2F, F7/F9), -110.8 - -110.9 (m, 2F, F7/F9), -131.2 - -131.3 (m, 2F, F8).

1-Benzyl-4-(3,3,4,4,5,5-hexafluoro-2-(5-(4-methoxyphenyl)-2-methylthiophene-3-yl)cyclopent-1-ene-1-yl)-1H-1,2,3-triazole **(pF_{PS} 12)**



A microwave vial was heated under argon flow. Compound **6b** (150 mg, 0.373 mmol) was initially charged and dissolved in dry THF (1.6 mL). The solvent was degassed by flushing with argon under stirring and (azidomethyl)benzene **10a** (50 mg, 0.38 mmol) and copper(I)iodide (11 mg, 57 µmol) were added. The mixture was stirred for 5 min and then the catalyst phen$(PPh_3)_2Cu(I)NO_2$·DCM (4.6 mg, 5.3 µmol) was added before the vessel was sealed. The mixture was then stirred at room temperature overnight under light exclusion.
The mixture was transferred into a round-bottomed flask with diethyl ether and, after the addition of silica gel, the solvents were removed on a rotary evaporator. After the column chromatographic purification (silica gel, gradient: cyclohexane cyclohexane / ethylacetate 4:1), the product was obtained as a brown solid. 145 mg (73%).

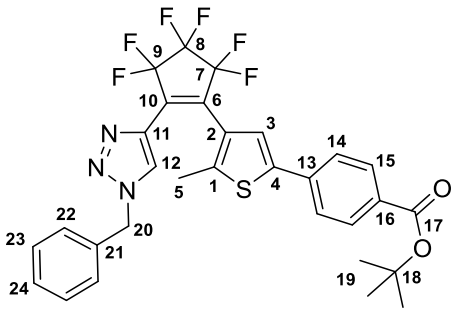
molecular weight: 535.51 g/mol
chemical formula: $C_{26}H_{19}F_6N_3OS$
exact mass 535.12, ESI-MS positive (m/z): 558.1031 (M+Na, calc. 558.1045)
1093.2162 (2M+Na, calc.1093.2400)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.44 (d, 2H, H15), 7.35-7.31 (m, 4H, H12, H21, H22), 7.22-7.18 (m, 2H, H20), 6.97 (s, 1H, H3), 6.91 (d, 2H, H14), 5.50 (s, 2H, H18), 3.85 (s, 3H, H17), 2.10 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 159.6 (C16), 142.8 (C13), 139.3 (C1), 136.7 (C11), 133.8 (C19), 129.4 (C21), 129.3 (C22), 128.3 (C20), 127.1 (C15), 126.4 (C4), 125.1 (C2), 124.8 (C12), 121.3 (C3), 114.5 (C14), 55.6 (C17), 54.6 (C16), 14.3 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.5 (m, 2F, F7/F9), -110.8 - -110.9 (m, 2F, F7/F9), -131.3 (m, 2F, F8).

tert-Butyl-4-(4-(2-(1-benzyl-1H-1,2,3-triazole-4-yl)-3,3,4,4,5,5-hexafluorcyclopent-1-ene-1-yl)-5-methyl-thiophene-2-yl)benzoate **(pF_{PS} 13)**



A microwave vial was heated under argon flow and compound **6d** (100 mg, 0.212 mmol) was dissolved in dry THF (1.0 mL). The solution was degassed by flushing with argon under stirring before (azidomethyl)benzene **10a** (31 mg, 0.23 mmol) and copper(I)iodide (6.6 mg, 35 µmol) were added in argon counterflow. The mixture was stirred for 30 min before the phen$(PPh_3)_2$Cu(I)NO_2·DCM catalyst (5.4 mg, 6.1 µmol) was added. The vessel was then closed and the mixture was stirred at room temperature overnight under light exclusion.
The solvent was removed on a rotary evaporator and the residue was purified by column chromatography (silica gel, gradient: cyclohexane cyclohexane / ethyl acetate 5:1). The product was obtained as a light orange solid. 51.0 mg (40%).

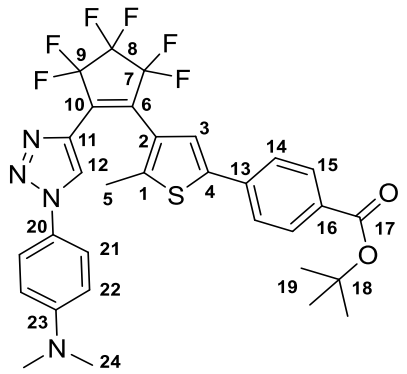
molecular weight: 605.60 g/mol
chemical formula: $C_{30}H_{25}F_6N_3O_2S$
exact mass 605.16, ESI-MS positive (m/z): 628.1456 (M+Na, calc. 628.1464)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.99 (d, 2H, H14), 7.56 (d, 2H, H15), 7.41 (s, 1H, H12), 7.36-7.32 (m, 3H, H23, H24), 7.23-7.20 (m, 3H, H22, H3), 5.51 (s, 2H, H20), 2.16 (s, 3H, H5), 1.61 (s, 9H, H19).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 165.5 (C17), 142.0 (C1), 141.4 (C4), 137.3 (C16), 136.2 (C11), 133.7 (C21), 131.2 (C13), 130.3 (C14), 129.5 (C23), 129.4 (C24), 128.3 (C22), 125.6 (C2), 125.2 (C12, C15), 123.9 (C3), 81.4 (C18), 54.6 (C20), 28.4 (C19), 14.5 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.3 - -110.4 (m, 2F, F7/F9), -110.9 - -111.0 (m, 2F, F7/F9), -131.3 - -131.4 (m, 2F, F8).

tert-Butyl 4-(4-(2-(1-(4-(dimethylamino)phenyl)-1H-1,2,3-triazole-4-yl)-3,3,4,4,5,5-hexafluoro-cyclopent-1-ene-1-yl)-5-methylthiophene-2-yl)benzoate **(pF$_{PS}$ 14)**



A microwave vial was heated under argon flow and compound **6d** (100 mg, 0.212 mmol) was dissolved in dry THF (1.0 mL). The solution was degassed by flushing with argon under stirring before 4-azido-N,N-dimethylaniline **10n** (38 mg, 0.23 mmol) was added in argon counterflow. Copper(I)iodide (6.6 mg, 35 µmol) was added and the vessel was then sealed. The mixture was stirred at room temperature for 30 min under light exclusion and then the catalyst phen$(PPh_3)_2Cu(I)NO_2$·DCM (5.4 mg, 6.2 µmol) was added. The vial was sealed and then stirred at room temperature for 2 days under light exclusion.
After the reaction control indicated an incomplete reaction, further Copper(I)iodide (6.6 mg, 35 µmol) and additional catalyst amounts of phen$(PPh_3)_2Cu(I)NO_2$·DCM (5.4 mg, 6.2 µmol) were added. The vessel was sealed again and the mixture was then stirred under protective gas for further 12 days.
The mixture was transferred into a round bottom flask and after the addition of silica gel, the solvents were removed on a rotary evaporator. After purification by column chromatography (silica gel, gradient: cyclohexane, cyclohexane / ethyl acetate 10:2), the product was obtained as a brownish solid. 25.0 mg (19%).

Due to small impurities, the NMR- and absorptions spectroscopic analytics were performed on a HPLC-purified sample.

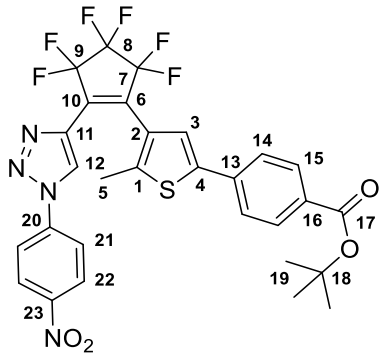
molecular weight: 634.64 g/mol
chemical formula: $C_{31}H_{28}F_6N_4O_2S$
exact mass 634.18, ESI-MS positive (m/z): 635.1880 (M+H, calc. 635.1880)
657.1715 (M+Na, calc. 657.1729)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 8.00-7.96 (m, 2H, H15), 7.91 (s, 1H, H12), 7.52-7.59 (m, 2H, H14), 7.49-7.46 (m, 2H, H21), 7.30 (s, 1H, H3), 6.77-6.72 (m, 2H, H22), 3.02 (s, 6H, H24), 2.28 (s, 3H, H5), 1.61 (s, 9H, H19).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 165.5 (C17), 151.0 (C23), 142.3 (C1), 141.3 (C4), 137.4 (C13), 136.2 (C11), 131.1 (C16), 130.3 (C15), 125.8 (C2,C20), 125.3 (C14), 124.0 (C3), 122.5 (C12), 122.1 (C21), 112.4 (C22), 81.3 (C18), 40.6 (C24), 28.7 (C19), 15.3 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.2 - -110.3 (m, 2F, F7/F9), -110.8 - -110.9 (m, 2F, F7/F9), -131.2 - -131.3 (m, 2F, F8).

tert-Butyl-4-(4-(3,3,4,4,5,5-hexafluoro-2-(1-(4-nitrophenyl)-1H-1,2,3-triazole-4-yl)cyclopent-1-ene-1-yl)-5-methylthiophene-2-yl)benzoate **(pF_{PS} 15)**



A microwave vial was heated under argon flow and compound **6d** (100 mg, 0.212 mmol) was dissolved in dry THF (1.0 mL). The solution was degassed by flushing with argon under stirring. Then 1-azido-4-nitrobenzene **10m** (50 mg, 0.31 mmol) and copper(I)iodide (6.6 mg, 35 µmol) were added in a protective gas countercurrent. After stirring for 30 min, the catalyst phen$(PPh_3)_2$Cu(I)NO_2·DCM (5.4 mg, 6.2 µmol) was added. The vessel was sealed and the mixture was then stirred at room temperature for 4 days under light exclusion.
The solvent was removed on a rotary evaporator and the residue was purified by column chromatography (silica gel, gradient: cyclohexane, cyclohexane / ethyl acetate 5:1). The product was obtained as an orange solid. 61.3 mg (46%).

Due to small impurities, the NMR- and absorption spectroscopic analytics were performed on a HPLC-purified sample.

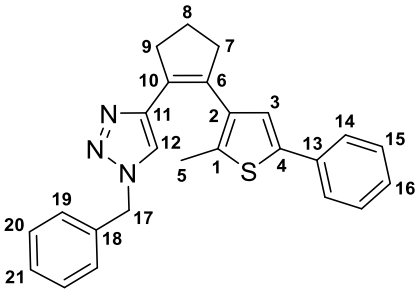
molecular weight: 636.57 g/mol
chemical formula: $C_{29}H_{22}F_6N_4O_4S$
exact mass 636.13, ESI-MS positive (m/z): 659.1172 (M+Na, calc. 659.1158)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 8.45-8.41 (m, 2H, H22), 8.21 (s, 1H, H12), 8.01-7.97 (m, 2H, H15), 7.96-7.93 (m, 2H, H21), 7.62-7.59 (m, 2H, H21), 7.31 (s, 1H, H3), 2.29 (s, 3H, H5), 1.61 (s, 9H, H19).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 165.4 (C17), 147.9 (C23), 142.5 (C1), 141.6 (C4), 140.3 (C16), 137.5 (C11), 137.2 (C13), 131.3 (C20), 130.3 (C15), 125.9 (C22), 125.3 (C14), 125.3 (C2), 123.8 (C3), 122.4 (C12), 121.0 (C21), 81.4 (C18), 28.4 (C19), 14.8 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -110.4 - -110.5 (m, 2F, F7/F9), -110.8 (m, 2F, F7/F9), -131.3 - -131.4 (m, 2F, F8).

1-Benzyl-4-(2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1H-1,2,3-triazole **(pH_{PS} 1)**



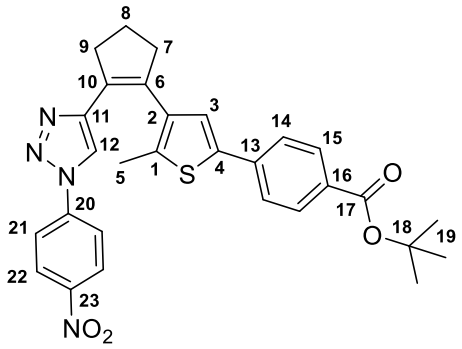
A microwave vial was heated under argon. Compound **9a** (33.0 mg, 0.125 mmol) was dissolved in dry THF (0.6 ml) and the solution was then degassed by flushing with argon under stirring. (Azidomethyl)benzene **10a** (18.3 mg, 0.137 mmol), copper(I)iodide (4.2 mg, 0.022 mmol) and phen(PPh_3)$_2$Cu(I)NO_2·DCM (1.9 mg, 2.2 µmol) were added. Then the reaction vessel was sealed and the mixture was stirred overnight at room temperature under light exclusion.
The solvent was then removed on a rotary evaporator and the residue was purified by column chromatography (silica gel, gradient: cyclohexane - cyclohexane / ethyl acetate 5:1). The product was obtained as a yellow, highly viscous oil. 45.0 mg (91%)

molecular weight: 397.54 g/mol
chemical formula: $C_{25}H_{23}N_3S$
exact mass 397.16, ESI-MS positive (m/z): 398.1678 (M+H, calc. 398.1685)
420.1506 (M+Na, calc. 420.1505)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.49-7.46 (m, 2H, H14), 7.37-7.33 (m, 2H, H15), 7.28-7.20 (m, 4H, H16,H20,H21), 7.15-7.10 (m, 2H, H19), 6.94 (s, 1H, H3), 6.83 (s, 1H, H12), 5.38 (s, 2H, H17), 3.13-3.08 (m, 2H, H9), 2.77-2.71 (m, 2H, H7), 2.13-2.05 (m, 2H, H8), 2.07 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 145.0 (C11), 141.1 (C4), 136.9 (C1), 135.2 (C6), 134.8 (C18), 134.4 (C13), 134.1 (C2), 130.4 (C10), 129.1 (C20), 129.0 (C15), 128.7 (C21), 128.0 (C19), 127.3 (C16), 125.4 (C14), 123.5 (C3), 120.7 (C12), 54.1 (C17), 39.3 (C7), 35.0 (C9), 22.7 (C8), 14.0 (C5).

tert-Butyl-4-(5-methyl-4-(2-(1-(4-nitrophenyl)-1H-1,2,3-triazole-4-yl)cyclopent-1-ene-1-yl)thiophene-2-yl)benzoate **(pH_{PS} 2)**



A microwave vial was flooded with argon under heating. Copper(I)iodide (7.0 mg, 0.037 mmol) and phen(PPh_3)$_2$Cu(I)NO_2·DCM (3.0 mg, (3.44 µmol) were initially added and dissolved in dry THF (1 mL). The solution was degassed by flushing with argon under stirring and then compound **9b** (40.0 mg, 0.110 mmol) and 1-azido-4-nitrobenzene **10m** (23.5 mg, 0.143 mmol) were added in argon counterflow. The vessel was closed and the mixture was stirred overnight at room temperature under light exclusion.
The solvent was removed on a rotary evaporator and the residue was purified by column chromatography (silica gel, gradient: cyclohexane / ethyl acetate 1:0 - 5:1) as an orange-yellow solid. 21.0 mg (36%).

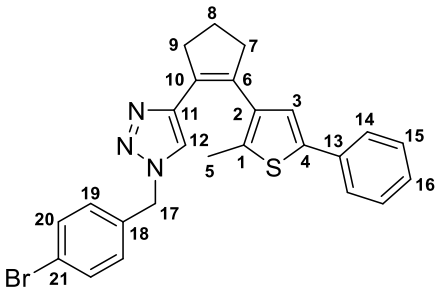
After column chromatography, minor impurities were still detected. Analysis of the photochrome reaction was performed on a HPLC purified sample.

molecular weight: 528.63 g/mol
chemical formula: $C_{29}H_{28}N_4O_4S$
exact mass 528.18, ESI-MS positive (m/z): 529.1961 (M+H, calc. 529.1904)
551.1780 (M+Na, calc. 551.1723)
1079.3690 (Mx2+Na, calc. 1079.3555)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 8.35-8.30 (m, 2H, H22), 7.99-7.95 (m, 2H, H15), 7.80-7.76 (m, 2H, H21), 7.62-7.57 (m, 2H, H14), 7.44 (s, 1H, H12), 7.19 (s, 1H, H3), 3.22-3.24 (m, 2H, 9), 2.88-2.81 (m, 2H, H7), 2.27 (s, 3H, H5), 2.22-2.14 (m, 2H, H8), 1.60 (s, 9H, H19).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 165.5 (C17), 147.2 (C23), 146.0 (C11), 141.2 (C20), 140.5 (C4), 137.9 (C13), 137.1 (C1), 136.9 (C10), 135.8 (C2), 130.8 (C16), 130.3 (C15), 129.6 (C6), 125.6 (C22), 124.9 (C14), 124.6 (C3), 120.4 (C21), 117.9 (C12), 81.3 (C18), 39.6 (C7), 35.2 (C9), 28.4 (C19), 22.6 (C8), 14.3 (C5).

1-(4-Bromobenzyl)-4-(2-(2-methyl-5-phenylthiophene-3-yl)cyclopent-1-ene-1-yl)-1H-1,2,3-triazole **(pH_{PS} 3)**



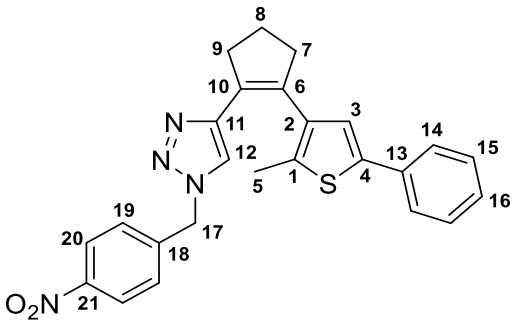
A microwave vial was heated in an argon stream and dry THF (0.3 mL) was degassed by flushing with argon under stirring. **9a** (10 mg, 0.038 mmol) was dissolved therein and then 1-(azidomethyl)-4-bromobenzene (**10b)** (5.9 mg, 0.04 mmol), copper(I) iodide (1 mg, 5 µmol) and $Phen(PPh_3)_2Cu(I)NO_2$·DCM (1 mg, 1 µmol) were added. The vessel was closed and the preparation was stirred overnight under exclusion of light at room temperature.
The solvent was removed on the rotary evaporator and the raw product was purified by column chromatography (cyclohexane/ethyl acetate 10:1). The product was obtained as a yellowish, glassy solid. Yield: 12.0 mg (67 %)

molecular weight: 476.44 g/mol
chemical formula: $C_{25}H_{22}BrN_3S$
exact mass 475.07, ESI-MS positive (m/z): 476.0740 (M+H, calc. 476.0796)
498.0595 (M+Na, calc. 498.0616)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.50-7.47 (m, 2H, H14), 7.39-7.32 (m, 4H, H15,H20), 7.29-7.25 (m, 1H, H16), 7.01-6.97 (m, 2H, H19), 6.95 (s, 1H, H3), 6.81 (s, 1H, H12), 5.33 (s, 2H, H17), 3.12-3.07 (m, 2H, H9), 2.78-2.72 (m, 2H, H7), 2.14-2.06 (m, 2H, H8), 2.10 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 145.2 (C11), 141.2 (C4), 136.9 (C1), 135.6 (C10), 134.3 (C13), 134.1 (C2), 133.9 (C18), 132.3 (C20), 130.3 (C6), 129.6 (C19), 129.1 (C15), 127.5 (C16), 125.4 (C14), 123.4 (C3), 122.9 (C21), 120.6 (C12), 53.3 (C17), 39.2 (C7), 34.9 (C9), 22.7 (C8), 14.0 (C5).

4-(2-(2-Methyl-5-phenylthiophene-3-yl)cyclopent-1-en-1-yl)-1-(4-nitrobenzyl)-1H-1,2,3-triazole **(pH_{PS} 4)**



A microwave vial was heated in an argon stream, **9a** (20 mg, 0.075 mmol) was placed in it and dissolved in dry THF (0.4 mL). The solution was degassed by flushing with argon under stirring. Then 1-(azidomethyl)-4-nitrobenzene (**10c)** (18 mg, 0.10 mmol), copper(I)-iodide (2.5 mg, 0.013 mmol) and the catalyst $Phen(PPh_3)_2Cu(I)NO_2 \cdot DCM$ (1.8 mg, 2.06 µmol) were added. The reaction vessel was closed and the preparation stirred under light exclusion at room temperature for 38 h.
The preparation was transferred to a round bottom flask with silica gel and the solvent was removed on the rotary evaporator. Column chromatographic purification (silica, gradient: cyclohexane/ethyl acetate 10:1 to 5:1) provided the product as a yellow solid. 19.0 mg (57 %).

molecular weight: 442.54 g/mol
chemical formula: $C_{25}H_{22}N_4O_2S$
exact mass 442.15, ESI-MS positive (m/z): 443.1545 (M+H, calc. 443.1536)
465.1356 (M+Na, calc. 465.1356)

^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 8.09-8.05 (m, 2H, H20), 7.47-7.43 (m, 2H, H14), 7.36-7.32 (m, 2H, H15), 7.28-7.23 (m, 3H, H16,H19), 6.93 (s, 1H, H3), 6.86 (s, 1H, H12), 5.49 (s, 2H, H17), 3.13-3.07 (m, 2H, H9), 2.78-2.73 (m, 2H, H7), 2.15-2.07 (m, 2H, H8), 2.14 (s, 3H, H5).

^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 145.5 (C11), 141.8 (C18), 141.3 (C4), 136.8 (C1), 136.2 (C10), 134.1 (C13), 134.1 (C2), 130.2 (C6), 129.1 (C15), 128.5 (C19), 127.6 (C16), 125.2 (C14), 124.3 (C20), 123.4 (C3), 120.8 (C12), 53.0 (C17), 39.2 (C7), 34.9 (C9), 22.7 (C8), 14.0 (C5).

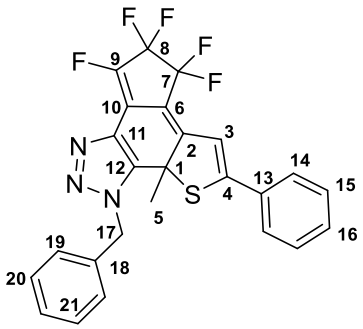
2.6.6. Isolation of the side product of pF_{PS} 1 in methanol

pF_{PS} 1 (4.34 mg, 8.59 µmol) was placed in a 500 mL Erlenmeyer flask (height 14.3 cm, ø 10.5 cm), dissolved in methanol (142 mL, approx. 60 µM) and an absorption spectrum was measured for reaction control. The radiation apparatus (MAX-303 Xenon Light Source 300W, Asahi Spectra USA Inc., with bandpass filter (ASA XHQA320), optical fiber (ASA QLG 1000) and collimator lens (x 0.5 type RLQL80-05) was set up (4 cm^2 area lighting on the surface of the solution, 2.5 cm above the bottom of the flask) A magnetic stirrer was used during the irradiation (320 nm) irradiated for 1 min, 2 min, 4 min, 10 and 20 min (total 100 min), and between the intervals, absorption spectra were measured as a control.
The chromatograms and the NMR spectrum of the crude product already showed a high level of purity. The product was nevertheless purified chromatographically using a pipette column (silica gel, cyclohexane). 3.71 mg (89%) of a yellow solid were obtained.

analytics:

ESI-MS positive: 508.0879 m/z (M+Na), (calculated for **pF-BP** (**pF_{PS} 1 - HF**) 508.0877 m/z).

The correlation of the NMR signals was referred onto the assumed structure **pF-BP** (see below and **Fig. S7**).



^{1}H-NMR (500 MHz, $CDCl_3$):
δ (ppm) = 7.60-7.55 (m, 2H, H14), 7.47-7.41 (m, 3H, H15,H16), 7.40-7.33 (m, 5H, H19,H20,H21), 6.90-6.87 (m, 1H, H3), 5.90 (d, 1H, H17a, $^2J_{H,H}$ = 15.5 Hz), 5.61 (d, 1H, H17b, $^2J_{H,H}$ = 15.5 Hz), 1.44 (s, 3H, H5).

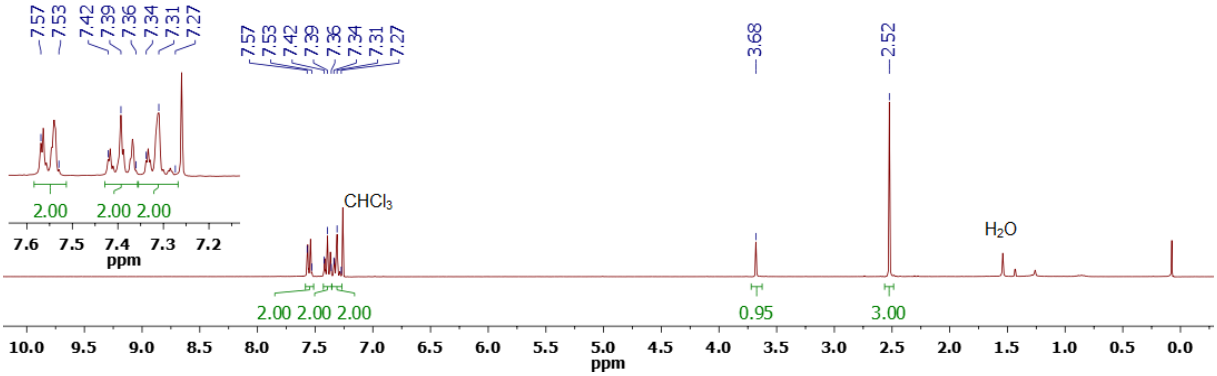
^{13}C-NMR (125 MHz, $CDCl_3$):
δ (ppm) = 151.5 (C4), 149.3 (C1), 138.7* (C12), 133.7 (C18), 133.1* (C11), 132.6 (C13), 130.8 (C16), 129.3 (C20), 129.2 (C21), 129.1 (C15), 128.0 (C19), 126.9 (C14), 112.4 (C3), 54.8 (C2), 53.3 (C17), 334.9 (C5).

^{19}F-NMR (282 MHz, $CDCl_3$):
δ (ppm) = -111.5 (dvm, 1F, F7a, $^2J_{F,F}$ = 253 Hz), -113.6 (dvdvm, 1F, F8a, $^2J_{F,F}$ = 254 Hz, $^3J_{F,F}$ = 15 Hz), -114.1 (dvm, 1F, F7b, $^2J_{F,F}$ = 253 Hz), -121.4 (dvdvm, 1F, F8b, $^2J_{F,F}$ = 254 Hz, $^3J_{F,F}$ = 15 Hz), -139.4 (tvm, 1F, F9, $^3J_{F,F}$ = 15 Hz).

3. NMR spectra

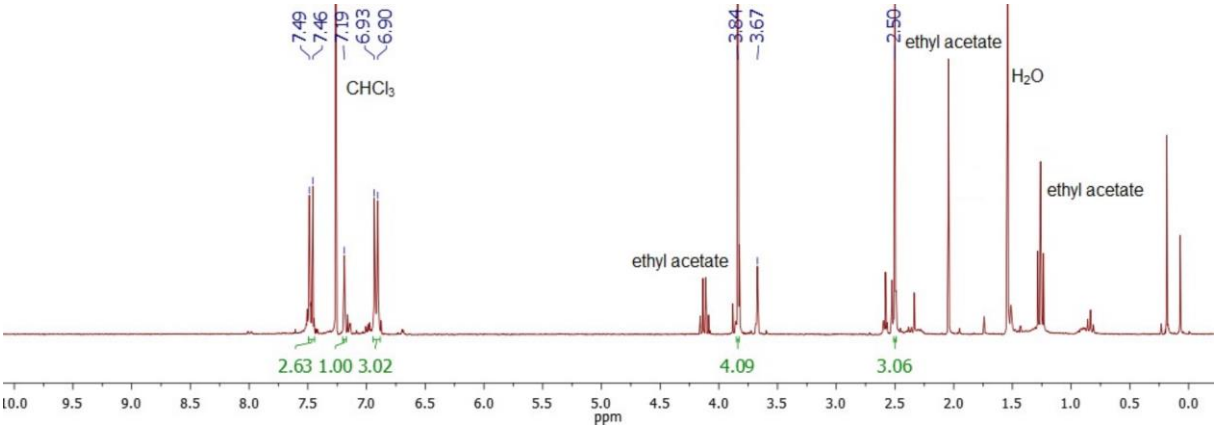
3.1. Acetylenes

Compound **6a**

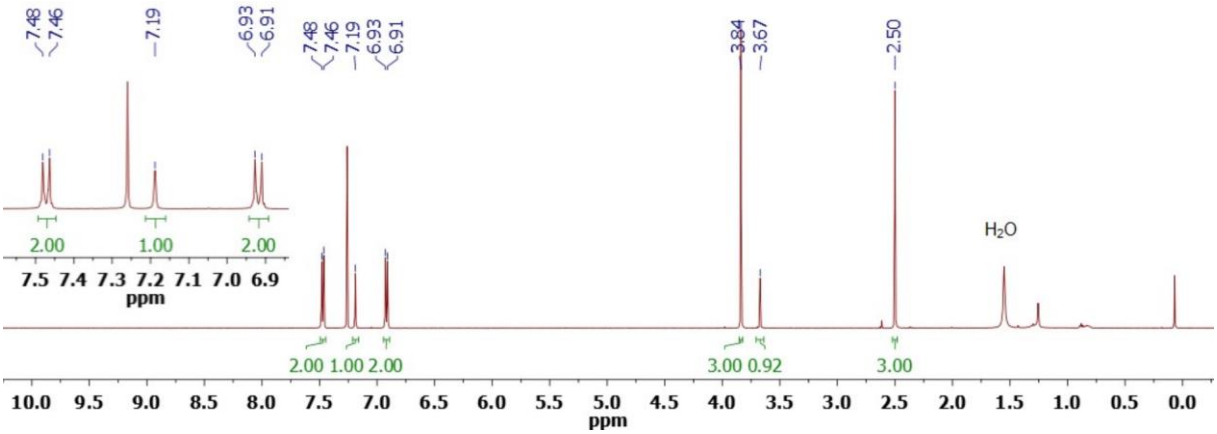


^{1}H NMR spectrum (300 MHz, $CDCl_3$)

Compound **6b**

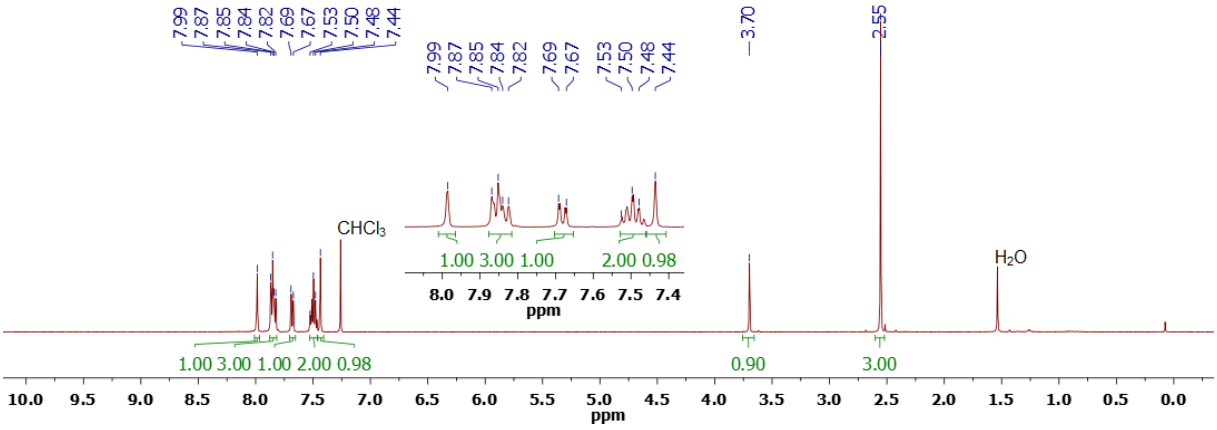


^{1}H NMR spectrum (300 MHz, $CDCl_3$), after column chromatography



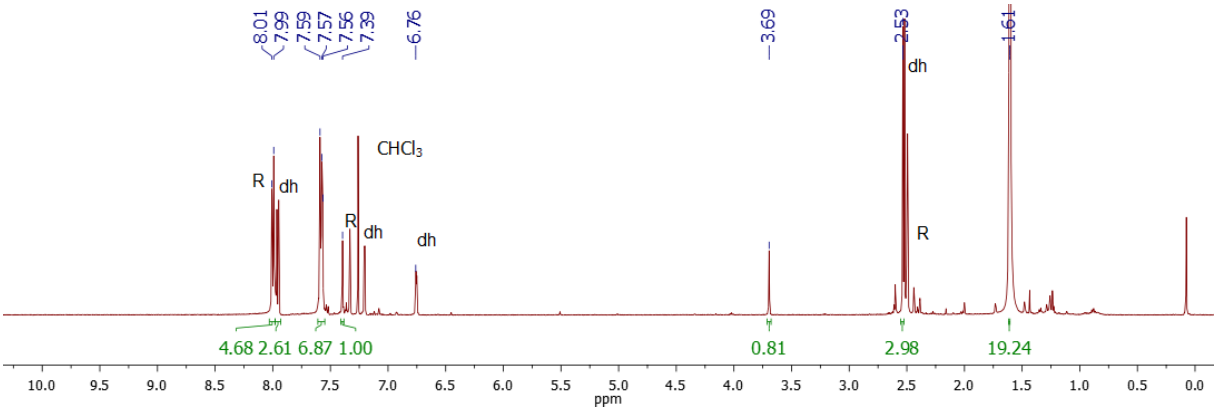
^{1}H NMR spectrum (500 MHz, $CDCl_3$), HPLC purified sample

Compound **6c**

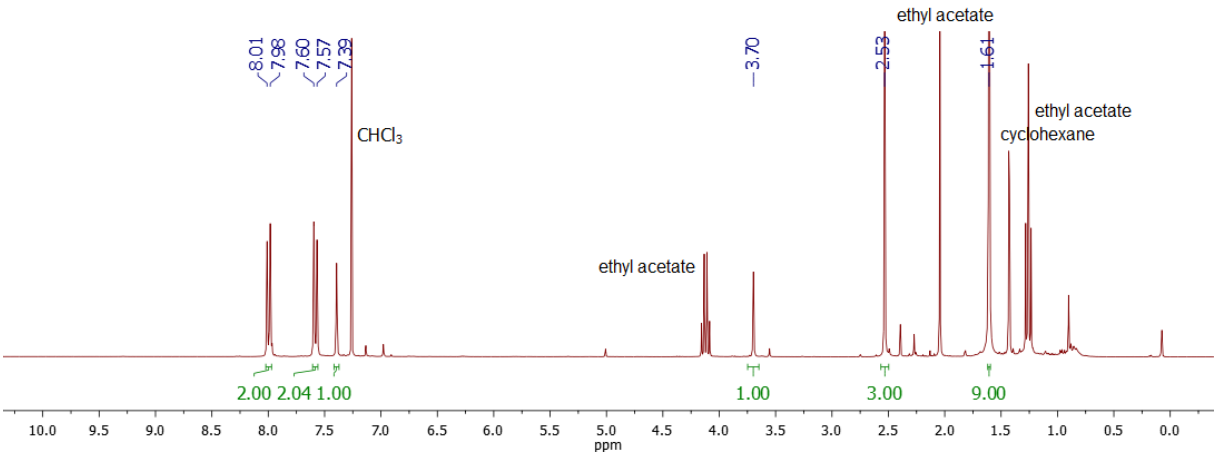


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **6d**

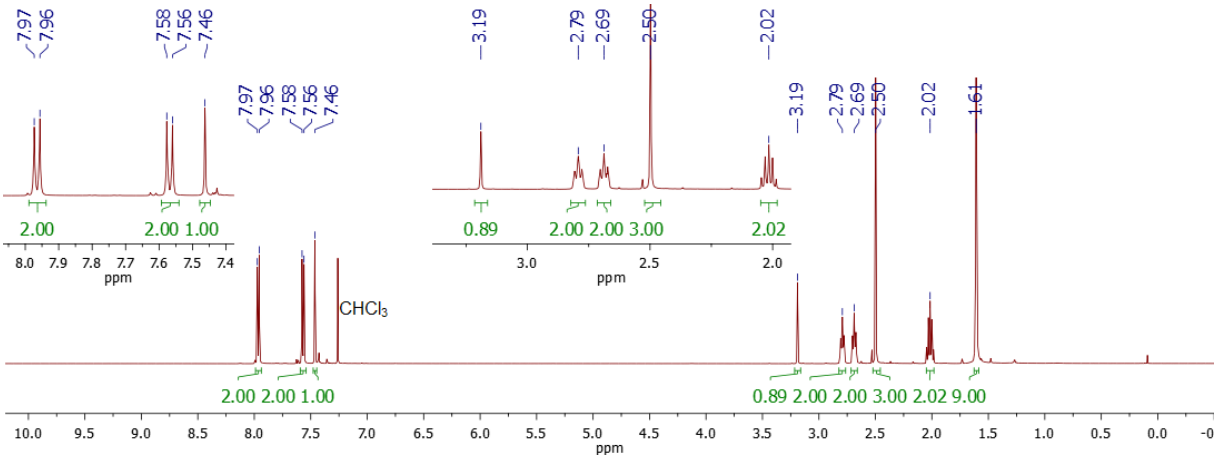


^{1}H NMR spectrum (500 MHz, $CDCl_3$), containing traces of reactant (R) and dehalogenated thiophene (dh) after column chromatography.



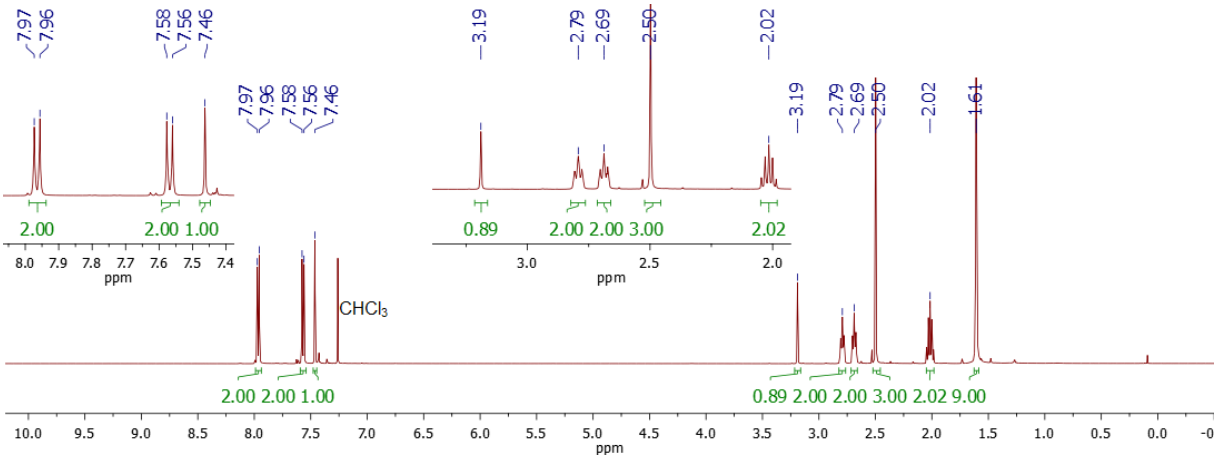
^{1}H NMR spectrum (300 MHz, $CDCl_3$), after HPLC purification.

Compound **9a**



^{1}H NMR spectrum (500 MHz, $CDCl_3$)

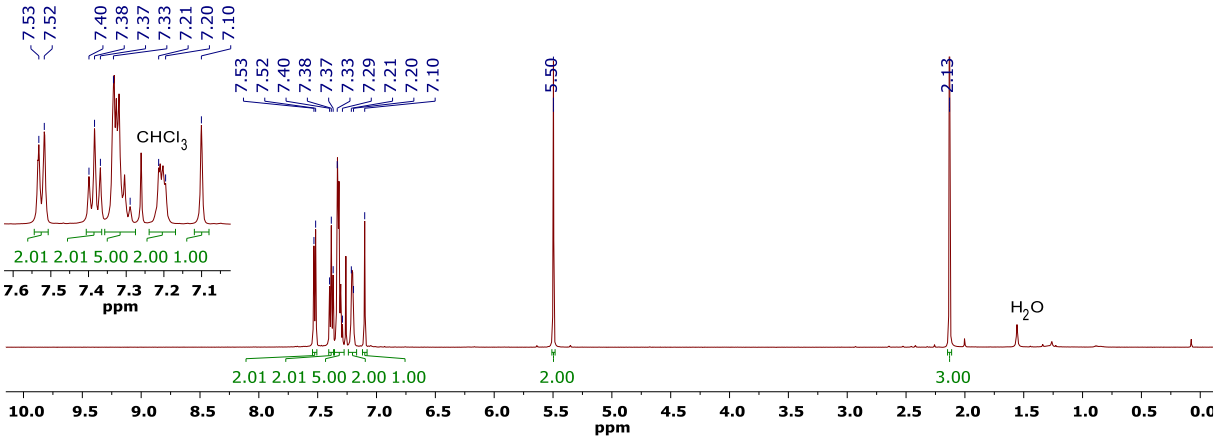
Compound **9b**



^{1}H NMR spectrum (500 MHz, $CDCl_3$)

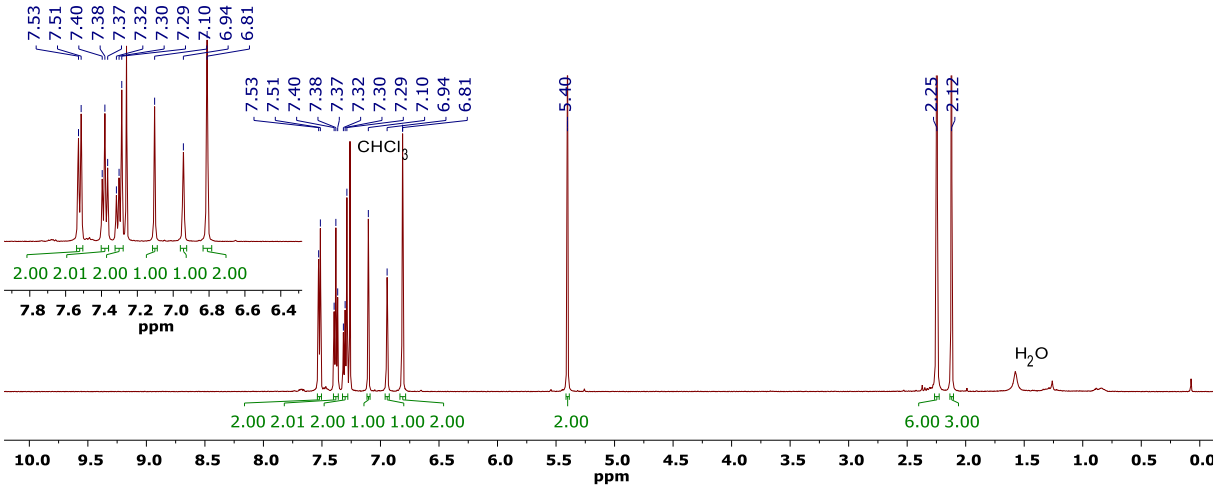
3.2. Triazole Photoswitches

Compound **pF$_{PS}$ 1**



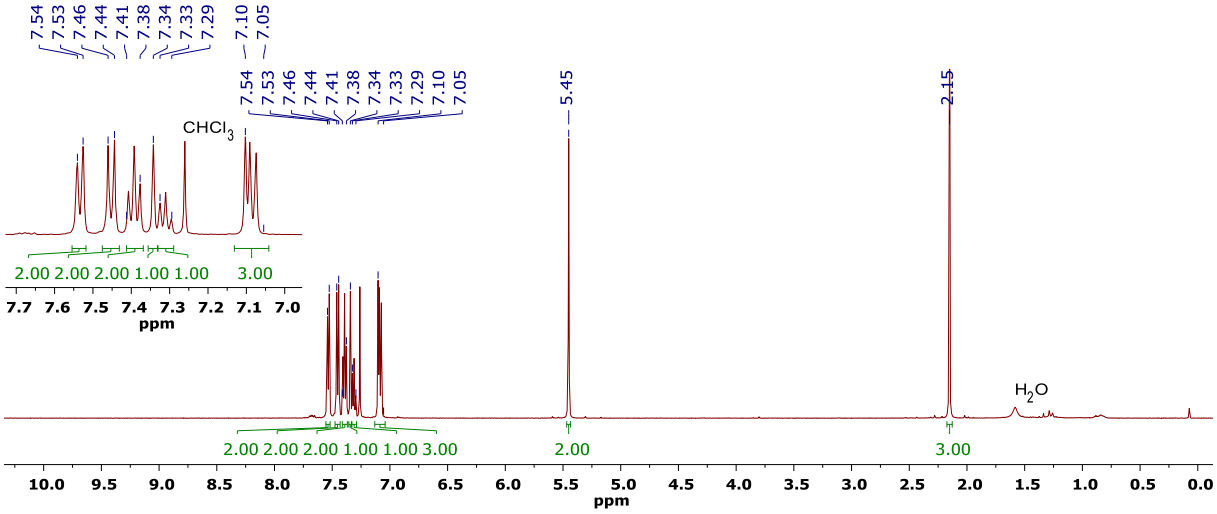
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF$_{PS}$ 2**



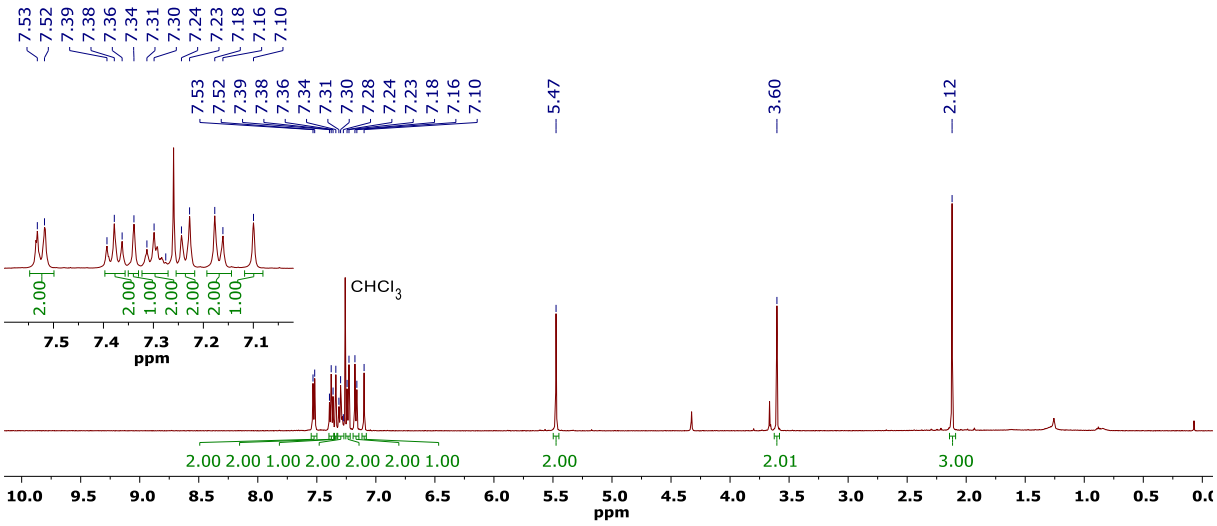
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 3**



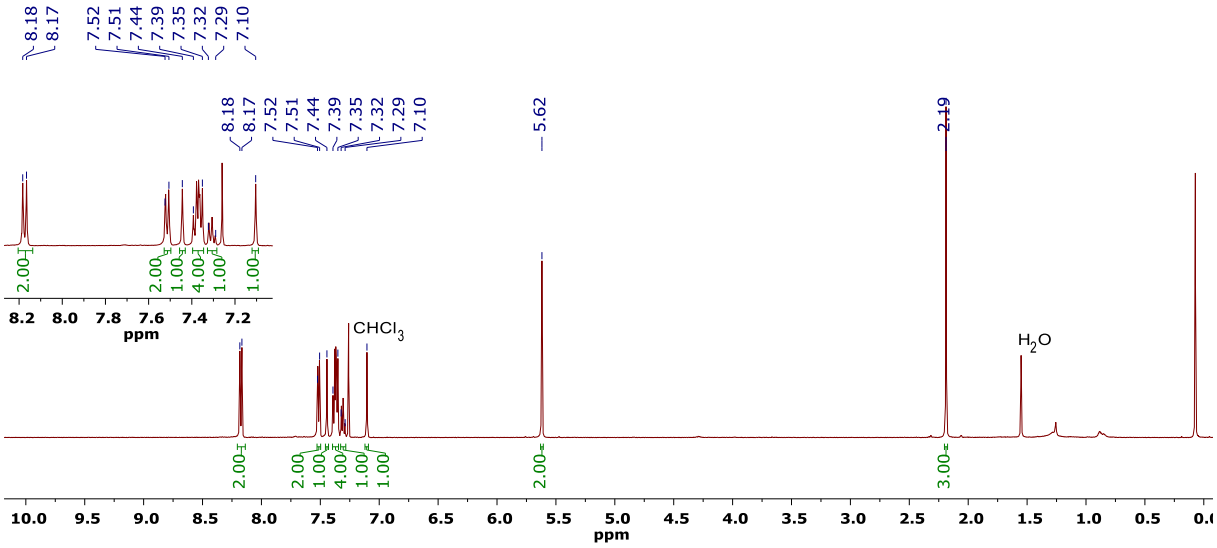
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 4**



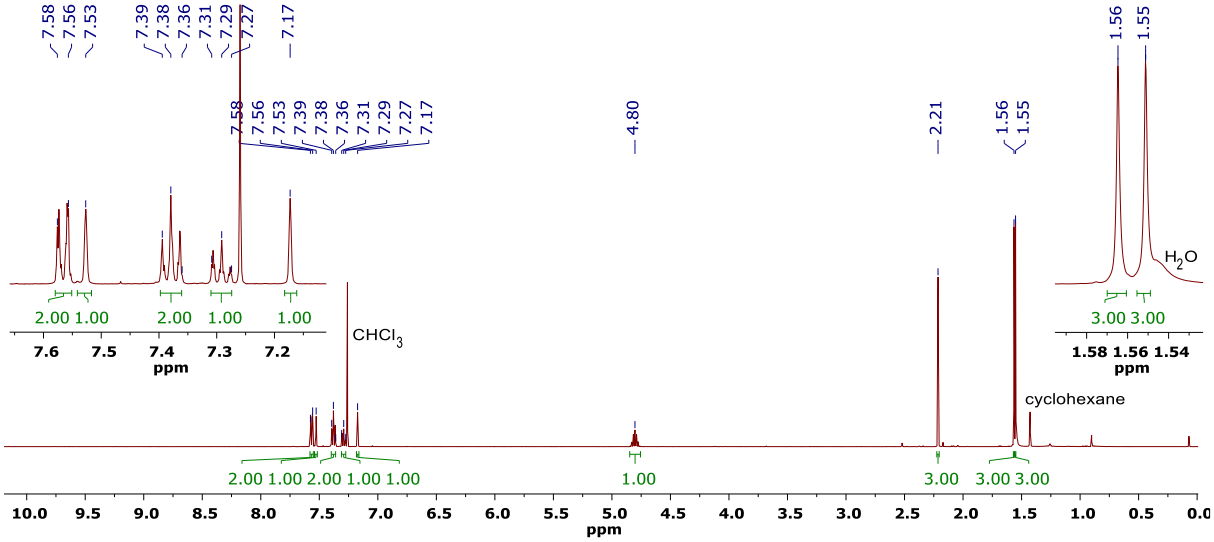
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 5**



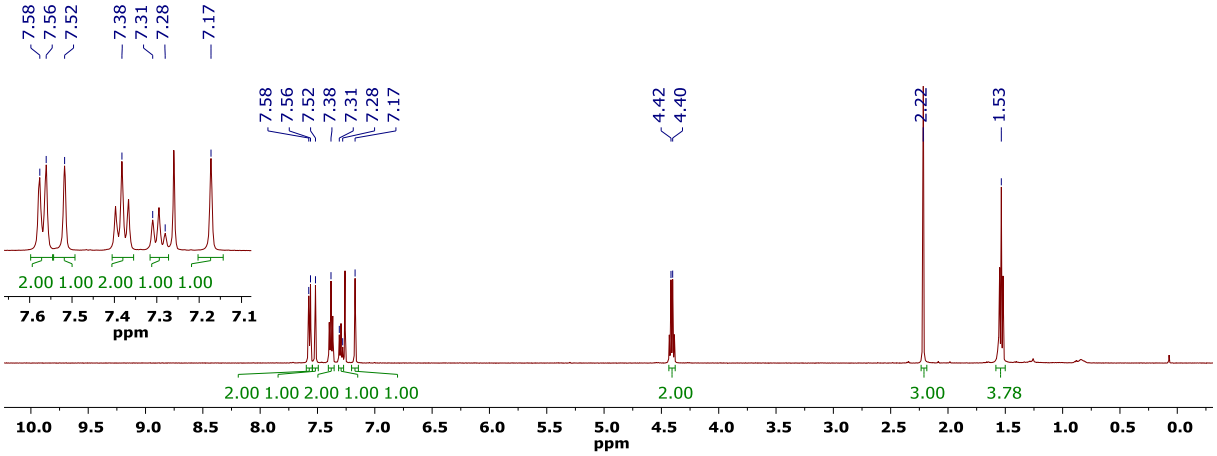
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 6**



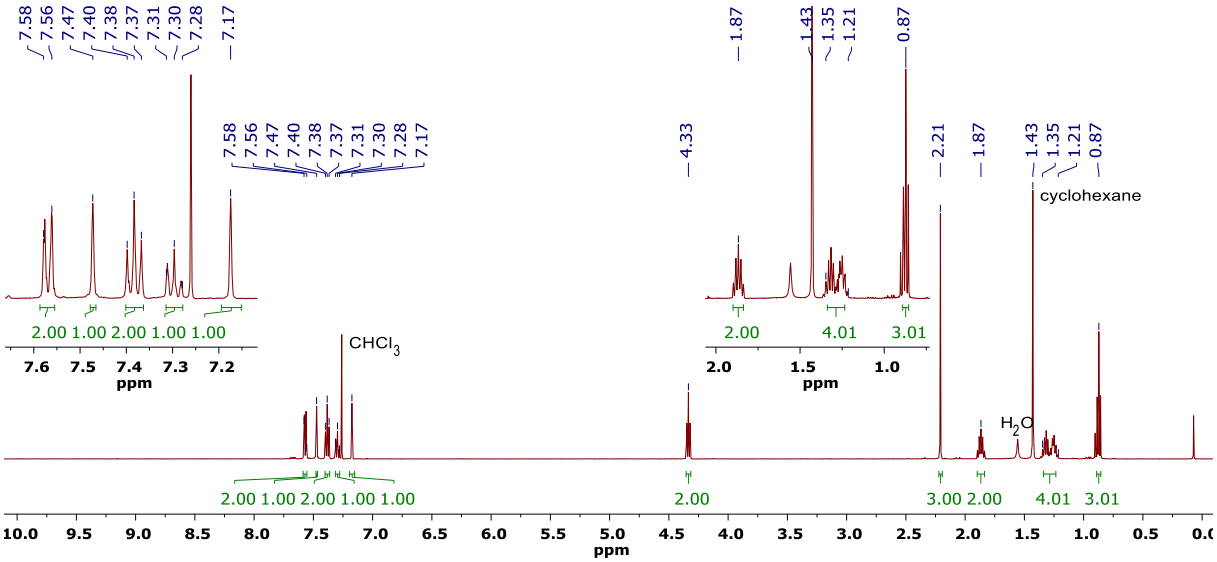
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 7**



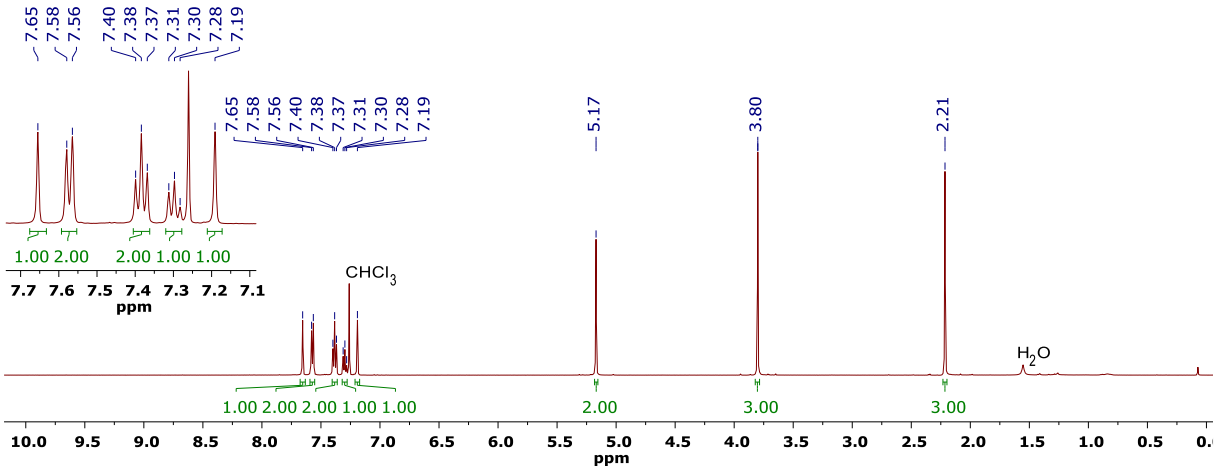
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 8**



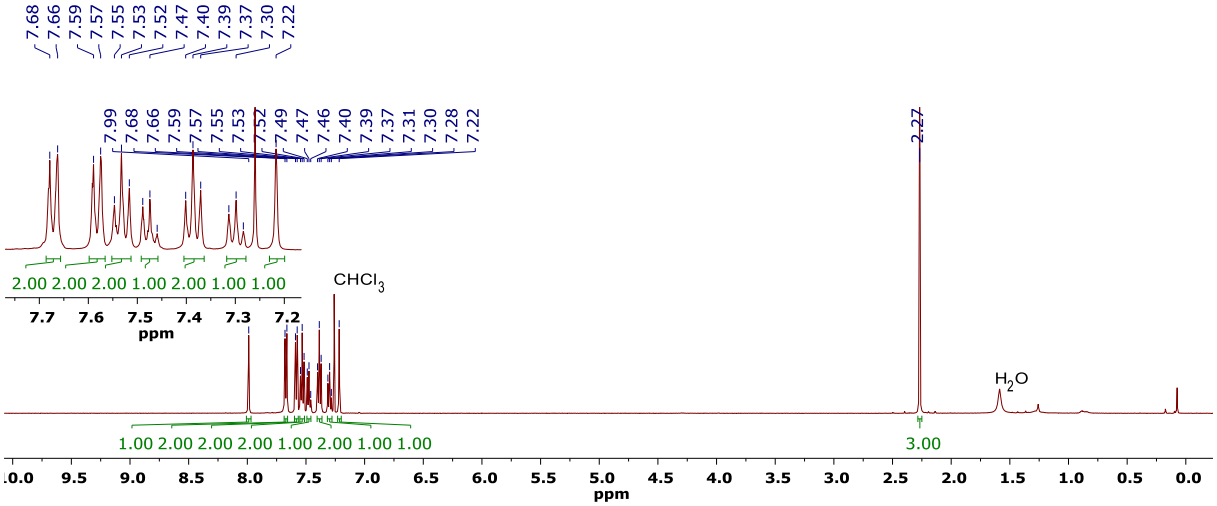
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 9**



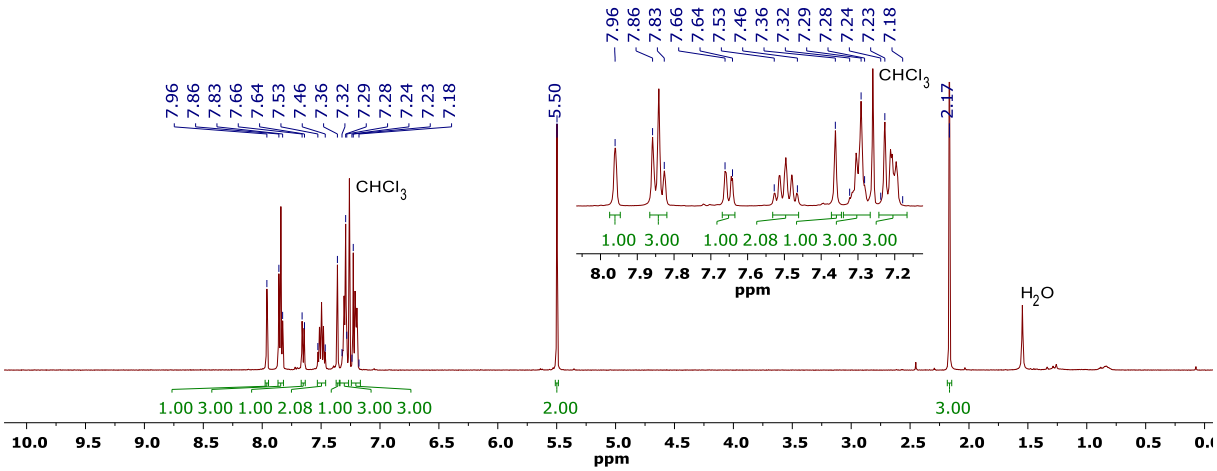
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 10**



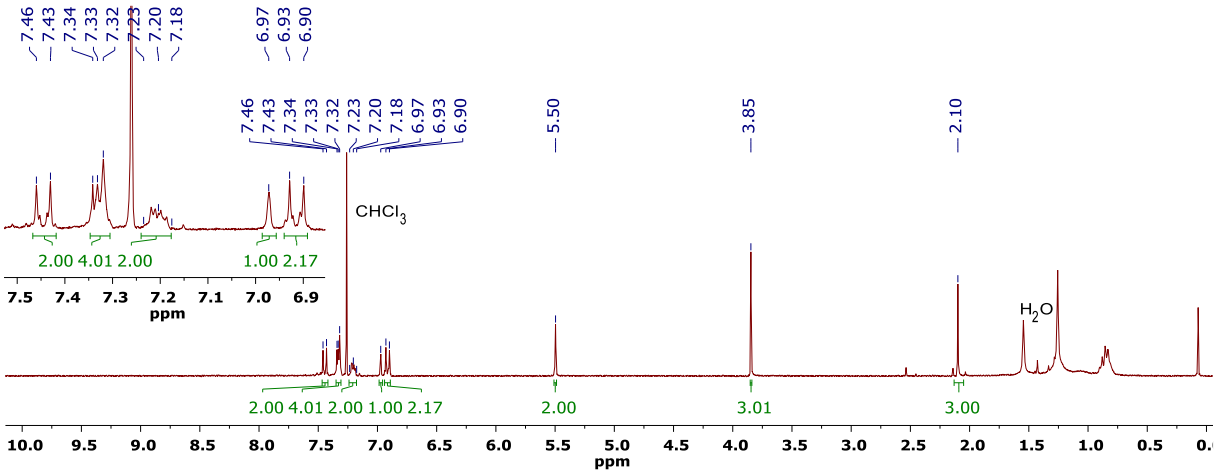
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 11**



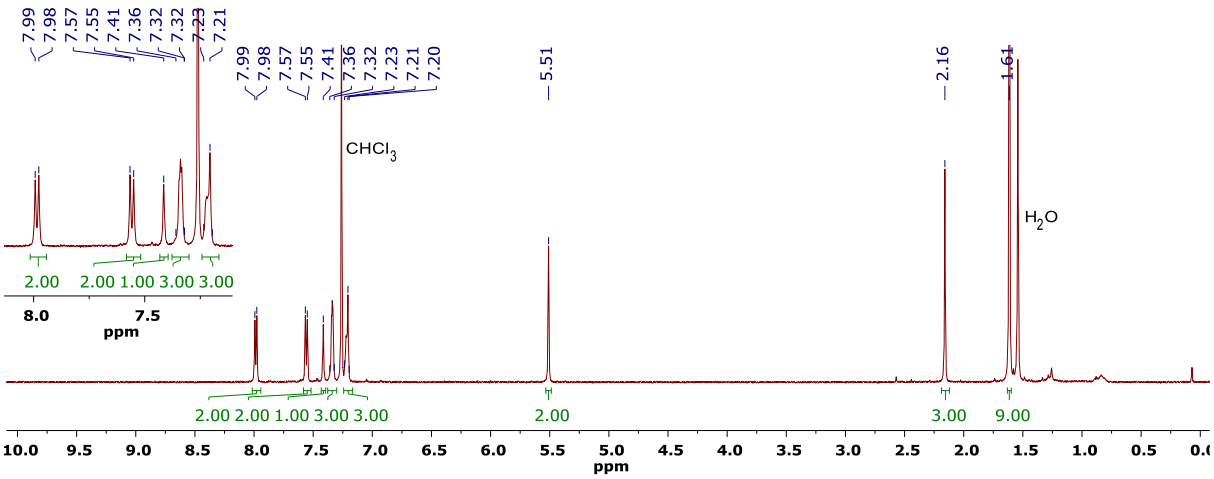
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 12**



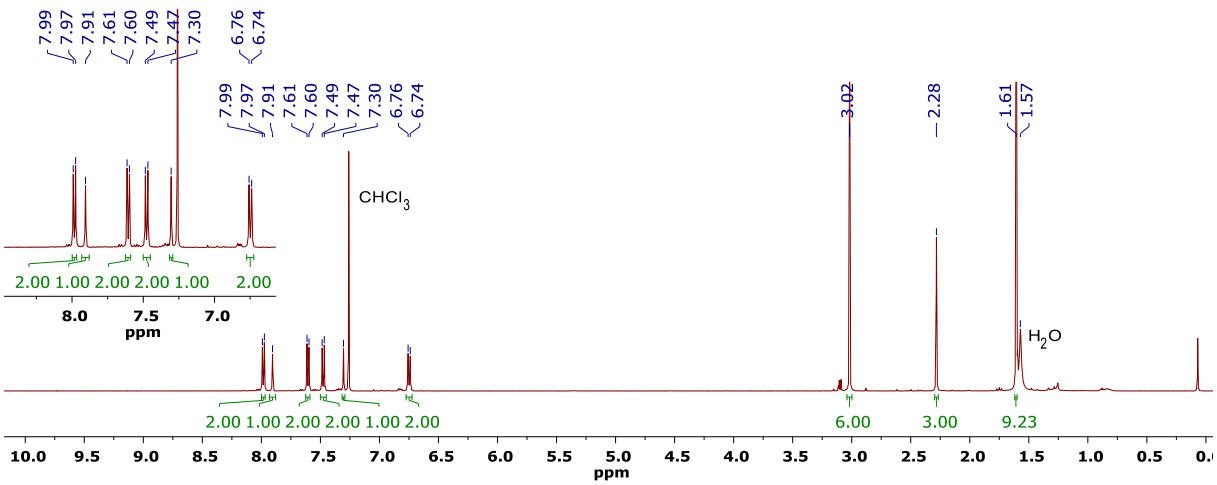
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 13**



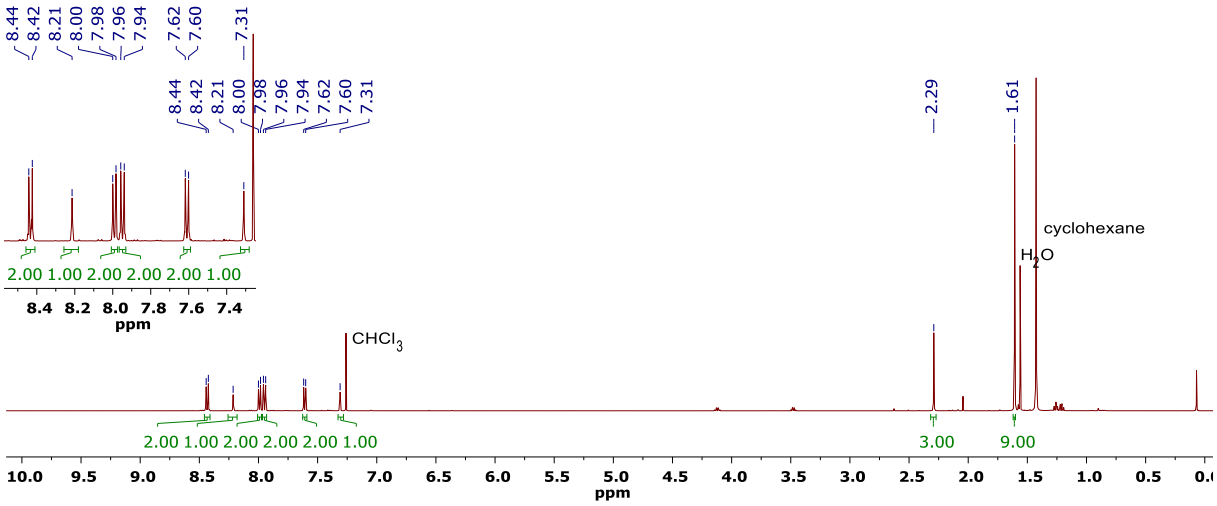
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 14**



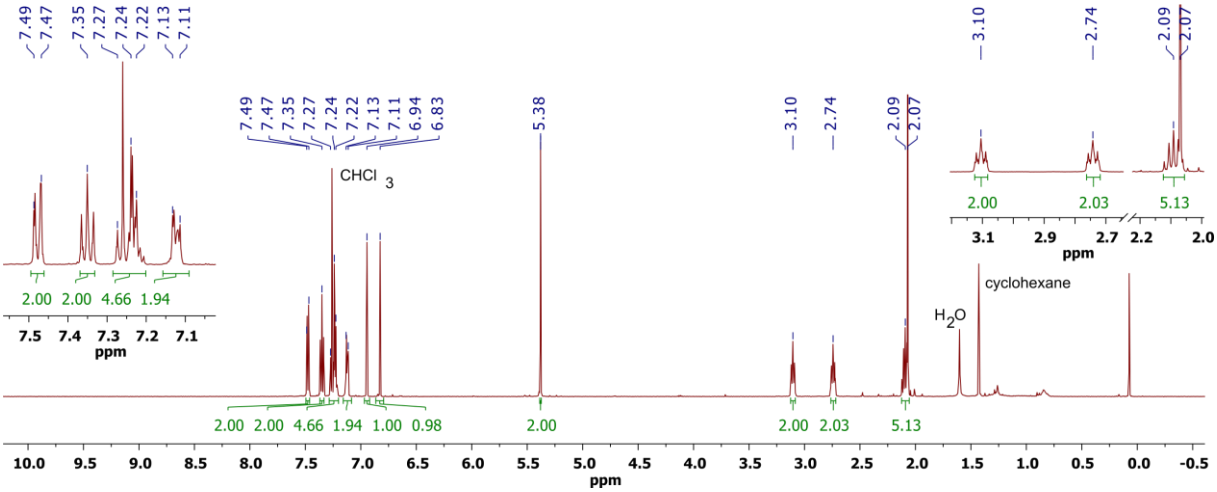
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pF_{PS} 15**



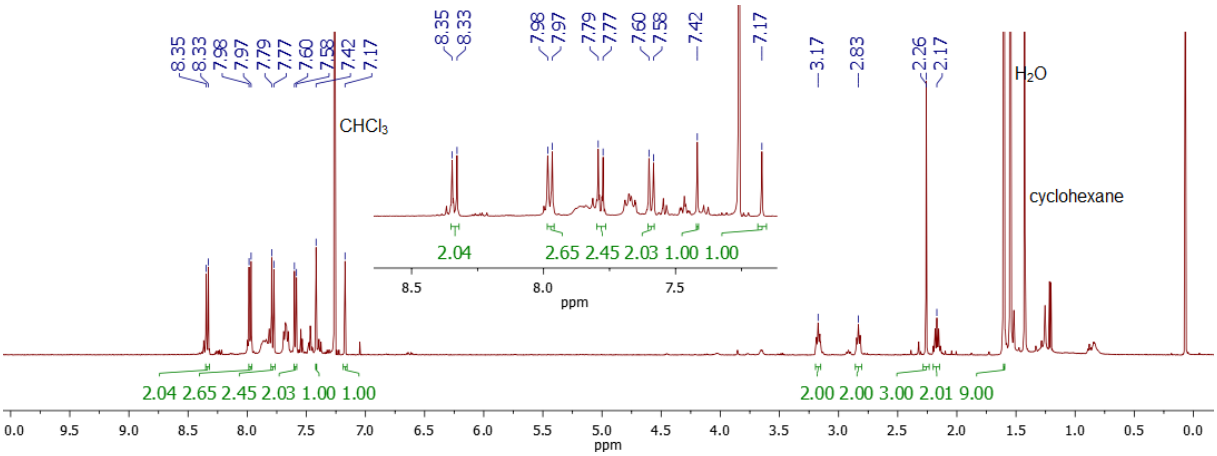
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pH_{PS} 1**

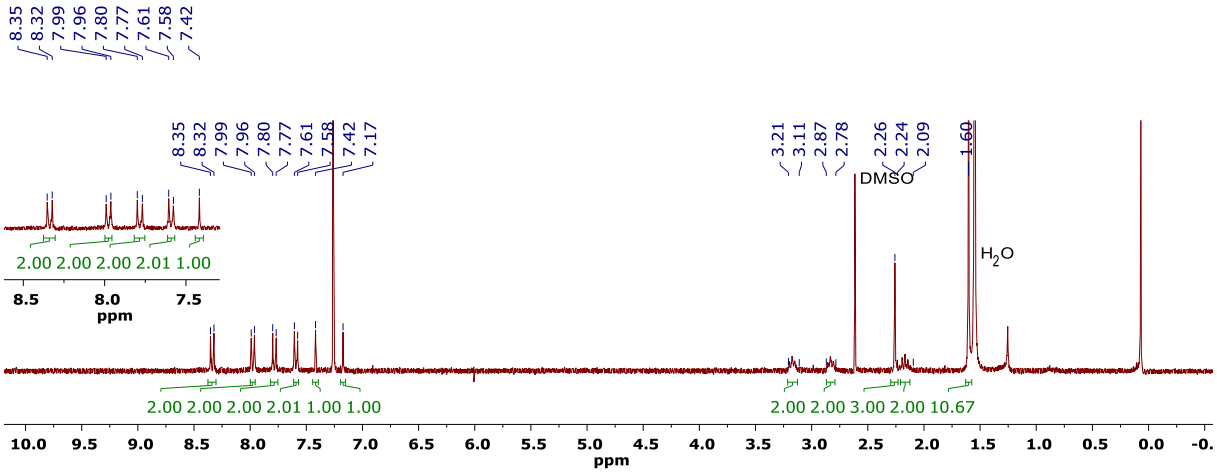


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pH_{PS} 2**

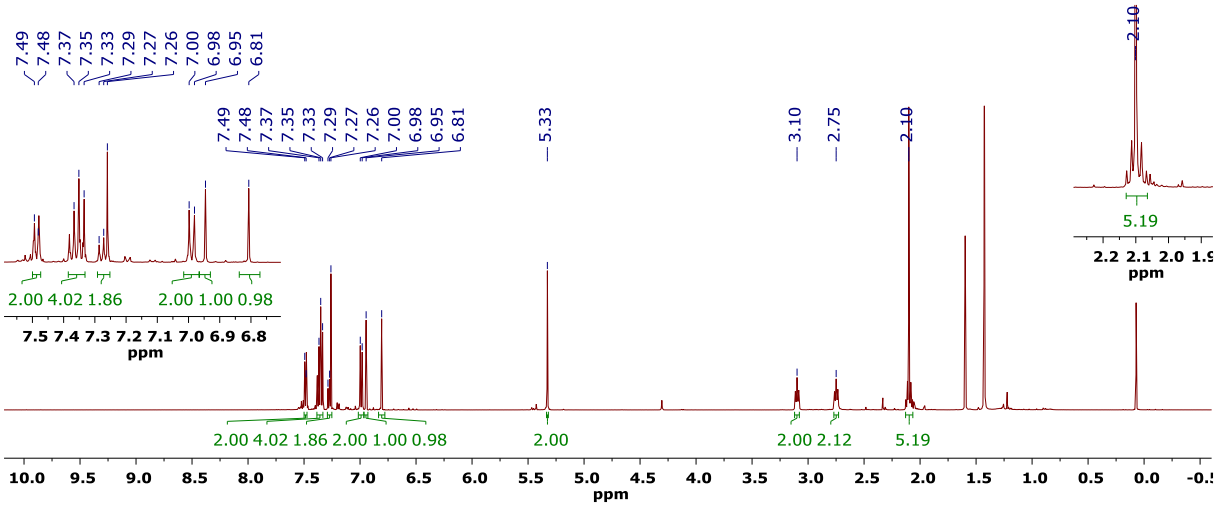


^{1}H NMR spectrum (500 MHz, $CDCl_3$), after column chromatography



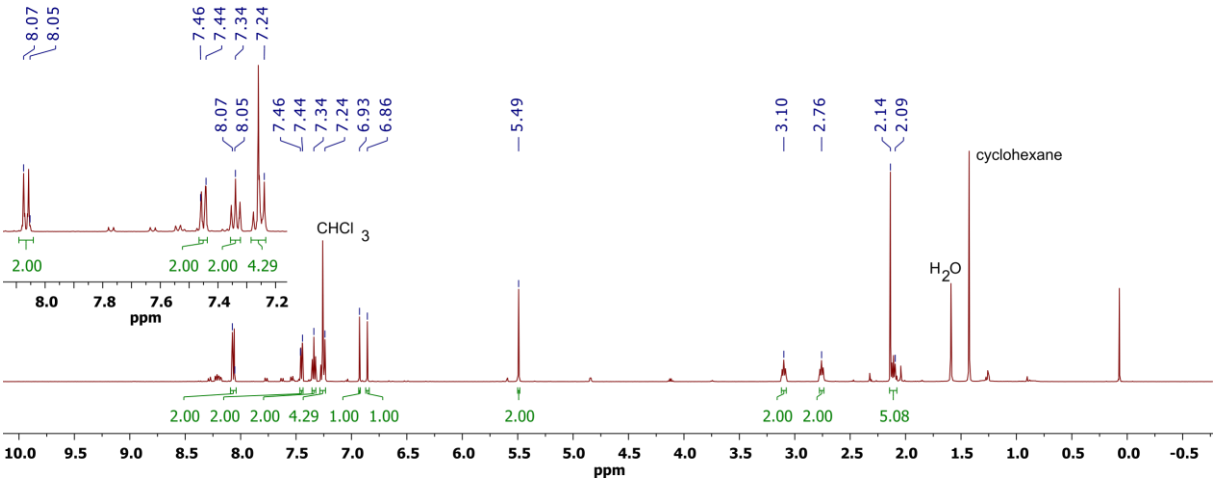
^{1}H NMR spectrum (300 MHz, $CDCl_3$), purified by HPLC

Compound **pH$_{PS}$ 3**



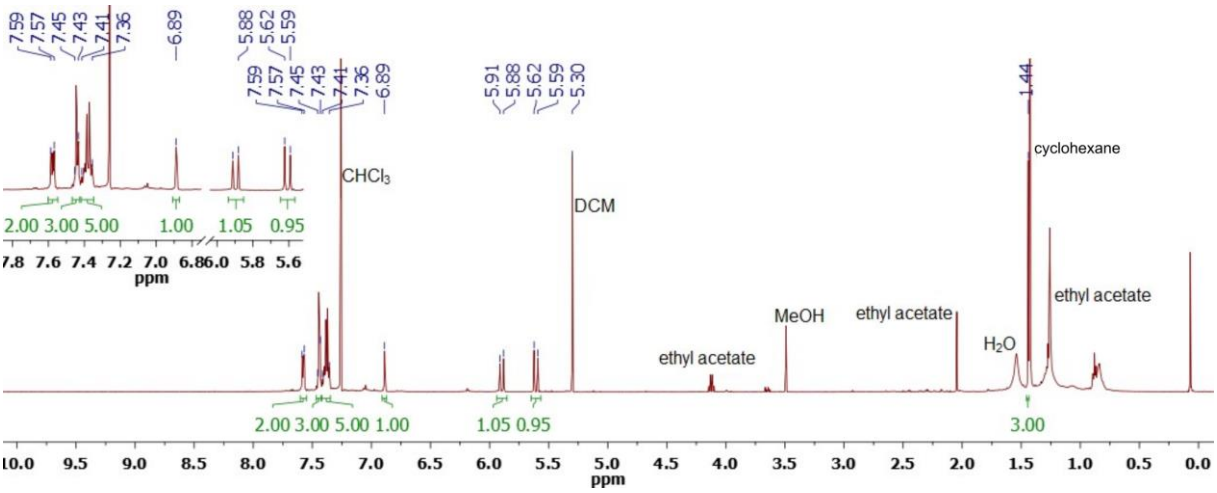
^{1}H NMR spectrum (500 MHz, $CDCl_3$)

Compound **pH$_{PS}$ 4**

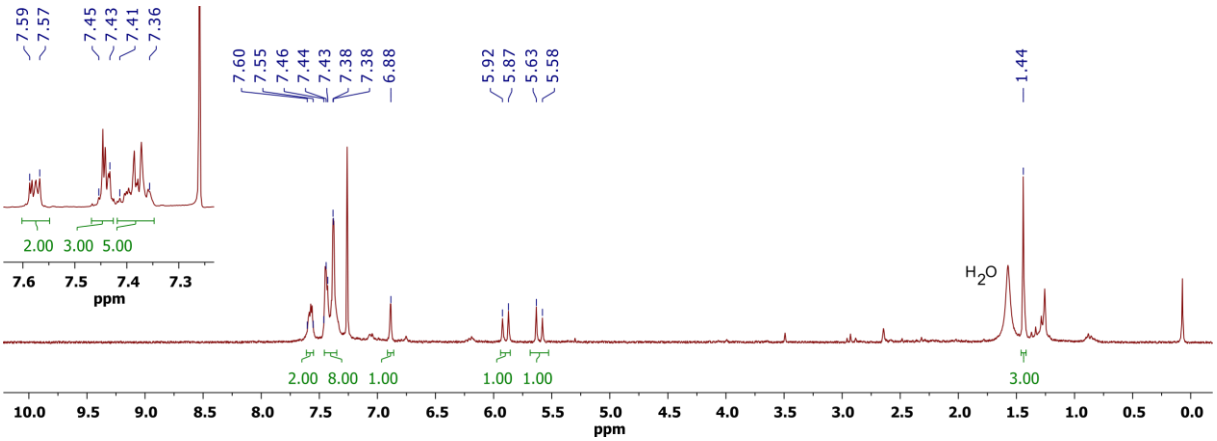


^{1}H NMR spectrum (500 MHz, $CDCl_3$)

3.3. **Side product of pF_{PS} 1 reaction in methanol (pF-BP assumed)**



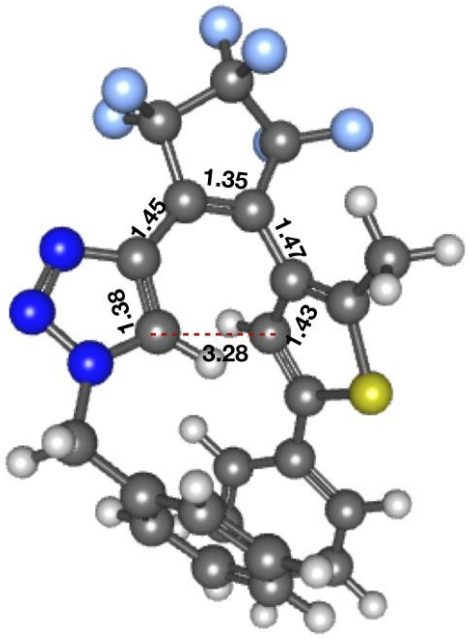
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



^{1}H NMR spectrum (300 MHz, $CDCl_3$), (small window: 500 MHz), purified via column chromatography

4. Computational details

Geometry of the optimized open form (all bond lengths in Angstrom):

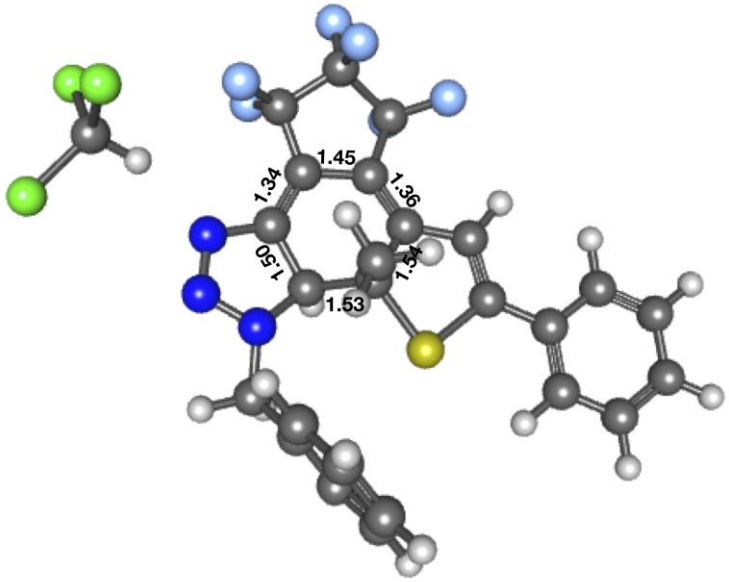


Equilibrium geometry of pF_{PS} 1 OF + 1 explicit $CHCl_3$ molecule:

C	1.4697606661	-1.5246426561	0.2260179160
C	0.1945391563	-1.7130068006	-0.2779114043
N	-0.1292466494	-2.9568955964	0.1129990286
C	2.3308544619	-0.3568024042	0.1437876006
N	1.8317240997	-2.6632443194	0.8817347783
N	0.8610831037	-3.5206580088	0.8122364570
C	3.8066639294	-0.4319754305	0.4305002533
C	1.9585437479	0.8996828944	-0.1662266259
C	3.1254781805	1.8413771583	-0.1390548757
C	4.3605428151	0.9088048328	-0.1224473681
C	0.5766504842	1.3319171838	-0.4347627969
C	-0.4123815134	1.4105217260	0.5962782650
C	0.0744809497	1.5377348878	-1.6952438968
S	-1.6381691929	1.8090060751	-1.6171440328
C	-1.6722601210	1.6571487573	0.1233990829
F	5.3731323984	1.3910028815	0.6111507183
F	4.7954280201	0.7220845462	-1.3854181882
F	3.1524463906	2.6795367616	-1.2021355261
F	3.1133006085	2.6230367595	0.9719923078
F	4.4108959521	-1.4868536163	-0.1556229567
F	4.0580111930	-0.5169512903	1.7622615141
H	-0.1739514513	1.2758628844	1.6507407408
C	-1.3580653604	-3.7129041331	-0.1643900624
C	-2.4726357619	-2.7958964735	-0.5988876709

C	-2.7258085621	-2.5893840906	-1.9582139691
H	-2.1353935394	-3.1260001517	-2.7046409486
C	-3.7210466420	-1.6996950133	-2.3625846520
H	-3.9093102256	-1.5415361998	-3.4260892768
C	-4.4705158835	-1.0118638321	-1.4085376049
H	-5.2458448905	-0.3102709533	-1.7216093271
C	-4.2272897667	-1.2181392309	-0.0503587552
H	-4.8071771692	-0.6742711911	0.6973956530
C	-3.2304644979	-2.1041776436	0.3525125519
H	-3.0328245328	-2.2564084978	1.4164584392
C	-2.9325059081	1.7412612102	0.8803723249
C	-4.0757410416	2.3436231477	0.3367825263
H	-4.0339022860	2.8039125211	-0.6531605344
C	-5.2741007165	2.3659540481	1.0471272703
H	-6.1542842270	2.8342078055	0.6029820613
C	-5.3485916149	1.7997852118	2.3196243367
H	-6.2874463709	1.8168037521	2.8757203521
C	-4.2115937923	1.2106141551	2.8759852652
H	-4.2579364956	0.7595360868	3.8689470739
C	-3.0172585781	1.1757524661	2.1623525205
H	-2.1484164627	0.6790182369	2.5967565820
H	-1.6087559837	-4.2465177269	0.7606859970
H	-1.1273379800	-4.4527014935	-0.9424914878
H	-0.4703609760	-1.0873000040	-0.8613200800
C	0.7987584919	1.4975516160	-3.0042654266
H	0.9023963733	2.5064707739	-3.4314365075
H	1.8068743132	1.0846767594	-2.8643807026
H	0.2655289483	0.8742999040	-3.7363249909
Cl	3.5312310287	-5.2394043966	3.1255093718
C	4.0668038097	-3.5453537547	2.9730935682
Cl	5.8072083547	-3.4671503436	2.6085208476
H	3.5029108475	-3.0981052765	2.1441597470
Cl	3.6845037692	-2.6301246140	4.4538486168

Equilibrium geometry of pF_{PS} 1 CF + 1 explicit $CHCl_3$ molecule:



C	1.88562553	-1.54137787	-0.06997550
C	0.39598490	-1.62409910	0.13333508
N	0.14138756	-2.78260101	-0.71767871
C	2.55954334	-0.43886844	0.30185988
N	2.31616032	-2.69117015	-0.72350950
N	1.29363555	-3.37831654	-1.04318864
C	4.02523405	-0.14105019	0.28636301
C	1.81429329	0.69144693	0.82684018
C	2.78086811	1.68312269	1.39000247
C	4.08846435	1.38382065	0.60183482
C	0.46775789	0.78298461	0.68536584
C	-0.43714333	1.78893060	1.15648661
C	-0.24882950	-0.27399477	-0.17319231
S	-2.01085957	-0.16949300	0.37360030
C	-1.74983485	1.44374741	1.06125491
F	5.19472083	1.72741394	1.27521350
F	4.05796623	2.07280429	-0.55846691
F	2.40982655	2.97594885	1.24867021
F	3.01905495	1.48360182	2.71656439
F	4.63170815	-0.41706771	-0.89131580
F	4.69988136	-0.82259746	1.24768420
H	-0.08446529	2.72032101	1.59410200
C	-1.02992832	-3.64273225	-0.60549838
C	-2.24279372	-3.10571207	-1.32849552
C	-2.14407246	-2.67643414	-2.65634871
H	-1.17921563	-2.72155262	-3.16735576
C	-3.26418520	-2.18702504	-3.32476269

H	-3.17341816	-1.84577140	-4.35769663
C	-4.49951058	-2.13549867	-2.67594809
H	-5.37682733	-1.74912859	-3.19788147
C	-4.60848529	-2.58057352	-1.35924536
H	-5.57112791	-2.54619947	-0.84571340
C	-3.48293126	-3.06096330	-0.68871698
H	-3.56796510	-3.39245295	0.34905284
C	-2.91232489	2.24522334	1.47908087
C	-4.21588623	1.73946607	1.35731767
H	-4.38259279	0.74341950	0.94158222
C	-5.31415895	2.49685390	1.75692681
H	-6.31885100	2.08363958	1.65461876
C	-5.12917324	3.77399045	2.28382137
H	-5.98898260	4.36941631	2.59567717
C	-3.83719782	4.28930815	2.40854272
H	-3.68383065	5.28893542	2.81850416
C	-2.73885859	3.53485688	2.01129990
H	-1.73988191	3.95978454	2.11428631
H	-1.25697174	-3.80170807	0.46158392
H	-0.72419506	-4.60956336	-1.02889198
H	0.17077015	-1.88356599	1.19167348
C	-0.14115644	0.14898635	-1.64793454
H	-0.55430223	1.15927276	-1.77080797
H	0.91250545	0.16124093	-1.96598237
H	-0.70107919	-0.54169692	-2.29039485
Cl	5.36091059	-2.42244508	-3.63220938
C	5.05869157	-3.41659341	-2.18480695
Cl	4.57411690	-5.06926489	-2.64515004
Cl	6.49175403	-3.44929355	-1.12886290
H	4.22175091	-2.97706383	-1.62767057

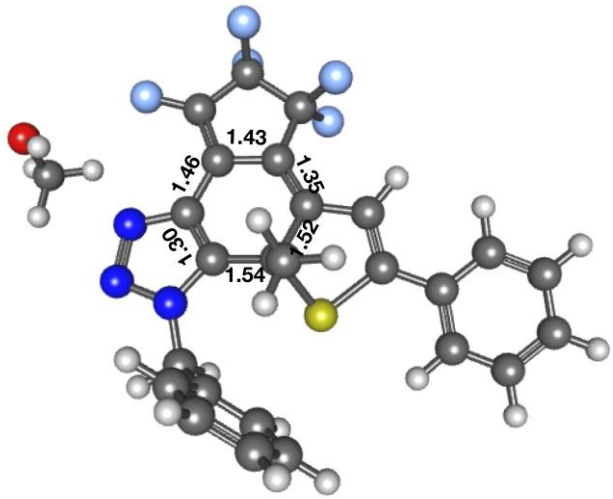
Equilibrium geometry of pF_{PS} 1: OF + 1 explicit MeOH molecule

C	1.5737102861	-1.4808243967	0.5349857438
C	0.3238854411	-1.7251746802	-0.0071531285
N	0.0043255035	-2.9489175328	0.4455786405
C	2.4149481591	-0.3005316071	0.4203316297
N	1.9243378800	-2.5703388285	1.2728701070
N	0.9714689859	-3.4504564871	1.2161675489
C	3.8841345021	-0.3266187769	0.7469039013
C	2.0218729167	0.9289388911	0.0371862204
C	3.1625207759	1.9024758141	0.0600890734
C	4.4191310180	1.0048747936	0.1530939565
C	0.6414711527	1.3115998942	-0.3042487467
C	-0.3851015103	1.4400127017	0.6846028909

C	0.1825198713	1.4190282357	-1.5932354366
S	-1.5364772200	1.6604736548	-1.5938413697
C	-1.6304465197	1.6284028835	0.1505601174
F	5.3963337544	1.5443605096	0.8966759128
F	4.8996982775	0.7793075183	-1.0866930166
F	3.2013877193	2.6983107543	-1.0344497084
F	3.0956523799	2.7284538021	1.1375166014
F	4.5284945799	-1.3858611567	0.2096548972
F	4.1091438547	-0.3557815025	2.0839737991
H	-0.1846073657	1.3821267557	1.7540128259
C	-1.2041547363	-3.7408371678	0.1711798969
C	-2.3080645379	-2.8745530733	-0.3795154986
C	-2.5055022107	-2.7814828185	-1.7607594757
H	-1.8747213633	-3.3649760808	-2.4355277133
C	-3.4972001387	-1.9466165395	-2.2758730146
H	-3.6425060262	-1.8776796898	-3.3555897793
C	-4.2988362164	-1.2004335492	-1.4117869221
H	-5.0719742030	-0.5422058241	-1.8125317616
C	-4.1101418852	-1.2932099989	-0.0321803788
H	-4.7318897124	-0.7047461927	0.6448592392
C	-3.1167623127	-2.1243913365	0.4817392310
H	-2.9621461996	-2.1873891041	1.5617755155
C	-2.9199618880	1.7376832955	0.8529545462
C	-4.0404899702	2.3173776834	0.2414218497
H	-3.9581387499	2.7430771282	-0.7615157902
C	-5.2670453294	2.3603361194	0.9012525633
H	-6.1295294552	2.8106075012	0.4066600930
C	-5.3919299907	1.8371529012	2.1884655208
H	-6.3530989862	1.8681926224	2.7046623950
C	-4.2775583476	1.2713241907	2.8115337306
H	-4.3646426741	0.8525176179	3.8158584147
C	-3.0543614250	1.2166140564	2.1497043415
H	-2.2023822590	0.7362320812	2.6336616100
H	-1.4914404114	-4.2063671483	1.1218917163
H	-0.9291822804	-4.5306931740	-0.5400071259
H	-0.3254875183	-1.1472257659	-0.6539511568
C	0.9536808679	1.2925493363	-2.8693104676
H	0.9747216179	2.2466941162	-3.4167526750
H	1.9902361065	1.0011805349	-2.6535305852
H	0.5094890518	0.5343293246	-3.5303594314
H	5.5165236612	-4.9602066097	2.2845176697
C	4.6727890183	-4.4208943185	1.8271421244
H	5.0380214784	-3.9476266439	0.8965938932
H	3.9060230691	-5.1690077213	1.5478213750
O	4.1965680456	-3.4793034929	2.7607818520

H 3.4350241686 -3.0428892998 2.3358065385

Equilibrium geometry of pF_{PS} 1: BP + 1 explicit MeOH molecule:



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C 0.5652812 -1.5819214 -0.5617357
N 0.2139369 -2.9113966 -0.9130924
C 2.5905823 -0.2921459 -0.2459056
N 2.3837250 -2.7579076 -0.9745456
N 1.3534677 -3.6792443 -1.2039070
C 3.9930390 -0.0324768 -0.1400678
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C 2.8062674 1.8659293 0.8246209
C 4.2352736 1.3161014 0.4723364
C 0.5198298 0.7902430 0.3381148
C -0.3160161 1.7739069 0.9951334
C -0.2991655 -0.3427987 -0.2702912
S -1.6723390 -0.5088954 0.9127171
C -1.5191874 1.2722626 1.2876611
F 5.0153809 1.1928534 1.6090160
F 4.8768741 2.1245426 -0.4495389
F 2.5761386 3.0893107 0.2191382
F 2.6357226 1.9778096 2.1945539
F 4.9684242 -0.8840748 -0.5395229
H 0.0149079 2.7778903 1.2118228
C -1.0768213 -3.5561841 -0.7236783
C -2.1819501 -3.0159201 -1.5900173
C -2.0558744 -2.9963214 -2.9891279
H -1.1514563 -3.3572864 -3.4619692
C -3.0998174 -2.4992060 -3.7795613
H -3.0000786 -2.4770421 -4.8565780
C -4.2738203 -2.0306476 -3.1804873

H	-5.0805092	-1.6477793	-3.7919888
C	-4.4099300	-2.0612744	-1.7915090
H	-5.3209399	-1.7057965	-1.3268153
C	-3.3720432	-2.5536612	-0.9988893
H	-3.4976946	-2.5790528	0.0762584
C	-2.6454824	2.0540337	1.8902002
C	-3.8949450	1.4324656	2.0973751
H	-4.0501270	0.3936455	1.8411356
C	-4.9693307	2.1519083	2.6272416
H	-5.9245872	1.6645763	2.7747997
C	-4.8162774	3.4971676	2.9605309
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C	-3.5875996	4.1280844	2.7651118
H	-3.4720098	5.1730127	3.0223810
C	-2.5070852	3.4177839	2.2325536
H	-1.5760513	3.9436098	2.0901355
H	-1.3499705	-3.4942841	0.3515058
H	-0.9710789	-4.6359046	-0.9669784
C	-0.8757681	0.1684102	-1.6074988
H	-1.4601176	1.1038971	-1.4741195
H	-0.0527823	0.3846211	-2.3234152
H	-1.5495523	-0.5629827	-2.0747322
H	6.0628796	-4.8918032	0.4886059
C	5.2846160	-4.3587373	-0.0950933
H	4.4564830	-5.0713996	-0.3003623
H	4.9247054	-3.4984949	0.5096583
O	5.8470719	-3.9087219	-1.2936060
H	5.1127567	-3.4629643	-1.7902042

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